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Glow discharge assisted vapour deposition of wear resistant titanium carbide coatings on steel.

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GLOW DISCHARGE ASSISTED VAPOUR
DEPOSITION OF WEAR RESISTANT TITANIUM
CARBIDE COATINGS ON STEEL

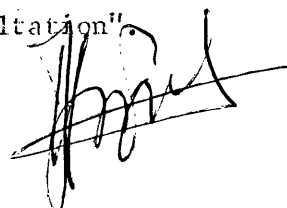
Submitted by P. C. Iordanis
for the degree of Doctor of Philosophy
of the University of Bath

1976

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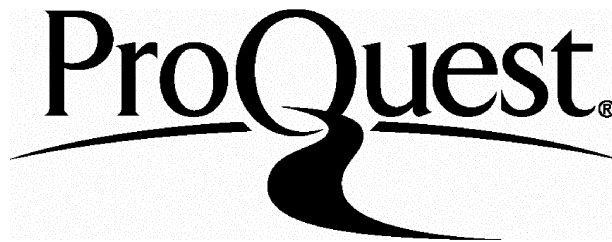
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SUMMARY

Deposition of TiC coatings is usually carried out by chemical vapour deposition. Recently deposition by sputtering and activated reactive evaporation has been reported. The ion plating technique (conventional and reactive), so far, does not seem to be successful. However, the present investigation using a third variation, chemical ion plating, produced adherent, uniform, dense, microcrystalline TiC coatings on steel substrates, characteristics expected when ion plating is used. Deposition took place on the cathode in an argon assisted glow discharge using gaseous reactants (TiCl_4 , C_2H_2 and H_2).

The parameters investigated were: the pressure, voltage and current of the discharge, the reactants ratio and indirectly the temperature of the substrate. It was found that the factor governing the deposition was the discharge current, heating the substrate to temperatures where the reaction is thermodynamically feasible.

The coatings were characterized by X-ray diffraction techniques. Their microstructure, thickness, uniformity and surface topography were studied by optical and scanning electron microscopy. The X-ray diffraction pattern showed only TiC with mean lattice parameter of $4.347 \pm 0.009 \text{ \AA}$ which is higher than the corresponding value in the literature (4.328 \AA) probably due to the stresses accumulated during deposition and the presence of Cl impurities. Electron probe microanalysis showed that the coatings consist of Ti, Cl (~4%) and C in greater than stoichiometric proportions, as was confirmed also by

chemical analysis. Oxygen was not detectable. The C was not detected as a second phase because it was non-crystalline and because the coating was very fine grained (below 1000 Å).

The properties of the coatings changed with composition. Vickers microhardness values reached 2700 - 3000 kgmm⁻², the values accepted for TiC, at high concentrations of C. The good adhesion between coatings and substrate, observed on qualitative basis, was assessed by the frequently used scratching test and was best at high C content. However, at high C contents partial spalling occurred which was avoided at low C contents or when carburized steel substrates were used. Deposition rate increased as the C content increased. Finally the friction coefficient of coatings against a stainless steel counterface decreased at high C contents (from 0.28 to 0.18).

CHAPTER I

1.1 GENERAL INTRODUCTION

Surface coatings are in use in nearly all branches of science and technology. The basic objective of any coating process is to extend the properties of the surface layer of the substrate material. By doing this common metals and alloys which do not have good surface resistance to corrosion, erosion, wear, etc. become resistant to attack by physical or chemical forces, and thus obtain durability which prolongs their functional life.

The more commonly known uses of surfaces coatings include the paint coatings the chromium plating on motor cars, the noble metals plating on jewellery and house utensils etc. There are uncountable further applications ranging from very thick copper coatings applied to printing rollers to very thin anti-reflection coatings on camera lenses; from high temperature diffusion coatings in jet engines to vacuum deposited resistors in electrical microcircuits and so on.

Coatings generally are classified into two categories: decorative and functional. Decorative coatings normally consist of that which is bright and shiny, usually silver or gold in appearance, although recently some applications of interference colours have been in use. In the case of functional coatings the increase of surface performance against corrosion, erosion and wear, and also the degree of the

improvement of the surface layer of the substrate according to the extent of the requirements of its use, comprises the guideline for the choice of the coating material and the coating technique.

The techniques used to coat surfaces are numerous; some examples of which are: hot dip galvanizing, hot dip tinning, carburizing, nitriding, porcelain enamelling, electroplating, anodising, cathodic sputtering, plasma spraying, chemical vapour deposition, ion plating, etc. The methods of coating can be classified either as physical or as chemical methods depending upon the mechanism which determines the deposition of the coating material onto the substrate, and also the bond strength created between coating and substrate. In the category of physical methods belong; hot dip galvanizing, hot dip tinning, porcelain enamelling, vacuum evaporation, cathodic sputtering, flame spraying, etc. In the category of chemical methods belong: electrolytic methods, carburizing, nitriding, chemical reduction, anodising, chemical vapour deposition, etc. Each of them serves a different purpose depending upon the nature of both the substrate and coating materials. The choice of a particular coating method is directed by economical and technical factors.

When the requirements of technology are mainly for protection of the substrate material, for example against corrosion or attack by acids, a coating deposited for instance by vacuum evaporation, where the adhesion depends mainly on relatively weak Van der Waals forces, (1), (2) it is suitable and satisfactory. As the technology progresses

and the requirements for coatings become more stringent, in order to work under more and more extreme conditions, for example working under conditions of wear and erosion simultaneously, proper coating materials should be developed to satisfy such requirements.

Basically, for optimum efficiency of a coating, its material should be compatible with the substrate material so that a matched pair is obtained. Simply putting a coating on to a material which, for example, has just failed to have adequate wear properties is rarely the best answer to a problem where wear is confronted. So by careful matching of the coating and the substrate materials it is possible to achieve a performance that neither material on its own would manage. In addition to this, a coating and its underlying substrate should "stick" together in such a way that they should be considered more as a composite material than as two separate entities.

This involves a very important property of the coatings, that which is referred to as adherence or adhesion. Each of the coating methods provides different grades of adhesion and this is dependent upon a number of different variables like the cleanliness of the substrate, its temperature, the compatibility of the substrate and coating material and also the acceleration and kinetic energy of the coating particles striking the substrate⁽³⁾. According to Spalvins⁽⁴⁾, of known deposition methods used today, ion plating offers the

highest potential in terms of film adhesion. Ion plating is the third member of the physical vapour deposition methods. The other two are vacuum evaporation and cathodic sputtering. Ion plating technique is described in detail in Chapter 3, while a general consideration of the other two methods, can be seen in Chapter 1.2.

These methods basically have the ability to deposit simple metal coatings on a substrate. However, non-metallic films of oxides, nitrides, etc. may be prepared indirectly by reactive evaporation or reactive sputtering. By using ion plating, metal coatings and alloys⁽⁵⁾ can readily be deposited. This method has also the ability of depositing non-metallic coatings like nitrides, carbides if evaporation and ionization of metals take place in the presence of active gases⁽⁶⁾.

In an attempt to study the feasibility of depositing a "hard" material like titanium carbide onto a steel substrate from the gas phase making use of the principles of the ion plating method, the basic intention of this investigation was to have:

- first a well adhered titanium carbide coating,
- second, a smooth surfaced coating, which would require minimum machining in the case of practical applications,
- third, a coating which would be deposited at temperatures below the softening temperature of steel thus avoiding substrate damage and
- fourth, a coating which is uniform all over the substrate (corners, recesses, blind holes, etc.)

Provided that it is possible using the ion plating technique to deposit titanium carbide on steel substrates from gas reactants, and that the coatings have the aforementioned good characteristics of this method, then it would be possible the good wear resistance of titanium carbide and the good fracture toughness of steel to be combined and thus practical applications like cutting tools, wear resistant precision engineers' gauges, protective coatings in high speed air bearings etc. could be met.

Titanium carbide, like most carbides, does not favour techniques like vacuum evaporation and conventional ion plating due to its high melting point, so the aim of the present work was to obtain titanium carbide coatings indirectly from the gas phase. Reasons which make the deposition of titanium carbide by the conventional ion plating unfavourable, as happens also with vacuum evaporation are the following.

During such methods the coating material, which is usually a simple metal, e.g. copper, is placed in a refractory boat such as tungsten which acts as the source providing the evaporant which will coat the substrate. In the case of ion plating the heater acts also as the anode, and the substrate as the cathode of the system. The evaporation may take place by thermal methods or electron beam techniques, for the more refractory materials. So it can be said that the ion plating is limited, as is vacuum evaporation, to

materials that can be easily evaporated.

As can be seen from Table 1⁽⁶⁾ the pure metals have comparatively low melting points compared with the alloys or the carbides and nitrides of the transition metals. Attainment of temperatures of about 1,500°C is comparatively straight forward, but production of temperatures significantly higher than this needs increasingly sophisticated equipment and instruments. Besides these problems it should be underlined that when alloys or compounds such as carbides nitrides, etc. are exposed under vacuum to the very high temperatures needed to melt them, they sometimes undergo decomposition and so the deposited materials are different to the intended ones.

Another technical problem which quite often appears during ion plating, as happens also in vacuum evaporation, is that when high temperatures are used for evaporating the coating material, the boat refractory material can soften and react with the semi-molten contents which could allow diffusion of their molecules and the final result is the creation of sintering, so that the ion plated coatings would be contaminated by atoms of the boat refractory materials.

The technical problems which are encountered by the conventional ion plating for depositing titanium carbide coatings directly from solid source of this compound may be overcome if the reactive ion plating method is used, which is described in Chapter 3. However, even this method is unfavourable for reasons which are summarized as

TABLE 1. Melting and Boiling Points of some Metals and Refractory Materials.

<u>MATERIAL</u>	<u>FORMULA</u>	<u>MELTING POINT °C</u>	<u>BOILING POINT °C</u>
Gold	Au	1064	2807
Copper	Cu	1083	2567
Nickel	Ni	1453	2732
Chromium	Cr	1857	2672
Chromium Carbide	Cr ₃ C ₂	1890	3800
Quartz	SiO ₂	2015	2590
Alumina	Al ₂ O ₃	2100	2980
Tungsten Carbide (Cobalt Alloy)	WC-Co	2695	6000
Silicon Carbide	SiC	2700	-
Titanium Nitride	TiN	2990	-
Titanium Carbide	TiC	3150	4820
Hafnium Carbide	HfC	3890	-

follows. Basically this method is a reactive evaporation method which takes place under ion plating conditions, and the reactive species present are the atoms of evaporated titanium and gas which is the carrier of carbon atoms. Due to the relatively high melting point of titanium (1,727°C) an electron beam is generally used to evaporate the material. Its evaporation by resistive heating, according to Holland⁽⁷⁾, leads to problems of filament failure and contamination of the deposit by atoms from the filament. The electron beam gun, however, is considered as a relatively sophisticated equipment, the original cost of which affects the economy of the method. Apart from this, the presence of the electron beam gun involves inherent technical problems. Ion plating operates at pressures above 1×10^{-3} Torr, while the electron emitting source operates best at pressures lower than 10^{-4} Torr. Thus, on the same unit should exist two spaces of different pressures and these spaces should be well isolated from each other so that the desired differential pressure is easily preserved. In this case the orifice connecting the two spaces should be as big as the size of the electron beam itself. Otherwise the pressure in the electron beam gun side rises and the electron-emitting filament degrades very quickly or even burns out. Furthermore, the gun should be assisted by an electrical system independent of that of the ion plating substrate holder and should be powered by a constant voltage high power unit at high potentials.

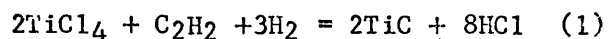
When large quantities of material need to be evaporated a movable ingot is employed which slides at its upper end into an annular water-cooled crucible. The ingot is normally continuously fed upwards into the crucible through a heat-resistant vacuum seal

in the chamber wall, at a controlled rate, to maintain constant melting pool height. So extra auxiliary devices are needed to assist the main ion plating apparatus.

Finally, the relevant investigations by Stowell⁽⁸⁾ discussed in more detail in Chapter 1.3, using this method to deposit titanium carbide coatings, led to the conclusion that coatings of a fine mixture of co-deposited titanium and carbon particles, were obtained instead of the intended carbide.

In order to overcome the technical problems of sophistication of the equipment and the inadequacy of the other two ion plating methods in giving titanium carbide coating a third variation of the ion plating method which would use only gaseous reactants, was chosen. The use of gaseous reactants does not require sources of high heating power and provides the ability of easy transportation into the reaction chamber since this is possible to be carried out in the same way as is done in the case of chemical vapour deposition. Such a method, utilizing principles of both the chemical vapour deposition and ion plating methods, may be called "chemical ion plating" as Mattox⁽⁹⁾ the originator of ion plating, is suggesting. The chosen gaseous reactants were titanium tetrachloride and acetylene, which were found to be the best reagents which could be used, as will be concluded from the further analysis of the present investigation. These chosen reactants were the carriers of the components of the intended coating, i.e. the volatile titanium tetrachloride was the carrier of titanium and

acetylene the carrier of carbon, for the titanium carbide coating. In this case these reactants were introduced into the reaction vessel as gases. A carrier gas (argon+5% hydrogen) was used to carry the titanium tetrachloride in the form of vapour. Thus, it can be seen that this method needs a simple system which does not use any other auxiliary equipment of high sophistication, since the only indispensable ones are those needed for the ion plating coating process and a thermostatically controlled water bath for heating the titanium tetrachloride. Finally, because the reactants are gases, control of the flowrates by means of flowmeters and needle valves provides the ability of very good control over the exact amount of each reactant at a time in the reaction zone. In the reaction zone and by the assistance of the glow discharge chemical synthesis according to the reaction,



occurs and the titanium carbide is deposited on the substrate.

Using the chemical ion plating process the amount of energy required to melt and evaporate either the titanium carbide or the titanium, as is necessary with the conventional ionplating or the reactive ion plating respectively, is saved. This amount of energy would be high, taking into account the boiling points of titanium carbide and titanium which are 4820°C and greater than 3000°C respectively. It must be made clear that the energy needed for the whole procedure of chemical ion plating of the titanium carbide is provided by electrical means. The applied potential between the electrodes provides the energy needed to start and sustain the glow discharge, the mechanism and the conditions of existence of which are discussed in Chapters 2 and 3. During the glow discharge and in-between the

electrodes in the plasma region the electron temperatures are about 10000°K or more as has been reported by some investigators^{(10),(11)}. Taking also into account the claims of Krutnant⁽¹²⁾ that during the ion plating process the energy input in watts to the substrate as a consequence of the electrical bias and resulting discharge is utilized mainly in heating the substrate and that approximately 95% of the kinetic energy of the ion bombardment is converted into heat, it can be said that the heating effect of the substrate is such that the formation of the coating compound is the result of the reaction taking place according to the details determined by the thermodynamics of the equation (1). Details of this are given in Appendix I. Finally another advantage of using ion plating process is the high purity of the obtained coatings since sources of contamination like heating coils or crucibles are avoided. So the purity of the coatings produced by chemical ion plating depends on the purity of the starting material and is not influenced by extraneous sources of contamination.

1.2. General Consideration of the Different Vapour Deposition Processes.

Many of the materials, being demanded by engineers and scientists as technology progresses, work under extreme conditions. However, the majority of the easily available metals and alloys have properties which are far below the required stringent specifications. A usual disadvantage of most of the metals and alloys is that they have small resistance to corrosion and wear. The reason for this is that, under usual conditions their surfaces are oxidized and the oxidation is propagating into the bulk because the formed surface oxide does not protect the bulk metallic material. The oxide is penetrable and easily removable. The deterioration of the oxidation is accelerated under conditions of damp and high temperature. Materials which are easily oxidised cannot be used in cases where mechanical wear is encountered because after obtaining a critical oxide film thickness this is removed from the surface of the metal by simple ploughing by a hard asperity.

For protection of metallic surfaces from oxidation and generally from corrosion or for improving the surface conditions towards wear, different kinds of coating methods are used, the choice of which comprises simultaneously an economical and technical problem.

By coating a substrate it is possible to extend the basic properties of the commonly available materials. The coatings can complement the properties of the substrate in order to achieve a

performance of which neither would be capable on its own. This is particularly true of wear resistant coatings. A hard material such as a carbide is too brittle to have any mechanical use on its own, but as a thin layer backed up by a steel it results in a combination of wear resistance and fracture toughness⁽¹³⁾.

Methods used for the application of different kinds of coatings are numerous. Among these it is possible to differentiate those which use liquid carriers such as baths of molten metals, molten salts, or diluted salts (methods of coating by hot dip, electroplating) and those which use gaseous carriers such as gases, volatile compounds or compounds which sublime under certain conditions (vacuum evaporation, chemical vapour deposition, sputtering, ion plating).

The objective of all these methods is to create on the native surface a protective film which is very thin in comparison to the thickness of the substrate, and which could be a simple metal or a chemical compound.

Below is an outline of the methods which utilize gaseous carriers because they are correlated with chemical ion plating method used in this project. In this way their differences are seen and compared.

1.2.1 Vacuum Evaporation

Evaporation in vacuo is a well established technique for depositing thin films of metals, alloys, semi-conductors, metal oxides and other oxides on various substrates (mainly insulators, plastic materials, and semi-conductors). Although this method provides

the ability for coatings of a wide spectrum of materials, however it cannot provide coatings of refractory metals and their carbides, borides, silicides. This is because the heating sources utilized (filaments or metal foil heaters) cannot withstand the high temperatures needed to vapourize these refractory materials. In addition it may be impossible to deposit film of such materials without undue heating of the receiving substrate. Another problem which appears in the case that a refractory compound is evaporated by this method, is its disintegration to its constituents and thus the possible coating may not be the intended compound but a mixture of its constituent atoms. However, this method is widely applicable in practice to deposit films of relatively low melting point materials. Both metals and thermally stable compounds begin to evaporate rapidly in high vacuum (10^{-5} - 10^{-6} Torr) when their temperature has been sufficiently raised for their vapour pressures to have reached a value in excess of 10×10^{-3} Torr ⁽⁷⁾. During the evaporation process, in equilibrium conditions, molecules are continuously passing from the condensed phase to the vapour phase but at the same time, another stream of molecules is condensing out of the vapour and the two processes balance each other.

The maximum possible rate of evaporation should occur if one could remove the vapour as fast as it is formed, the phenomenon however is not observable. Therefore the only way to calculate the evaporation rate is to utilize the fact that, in equilibrium, it is equal to the condensation rate, and the latter can be calculated from the kinetic theory of gases. The equation of the condensation rate R (in $\text{g.cm}^{-2}\text{sec}^{-1}$)

is that derived by Langmuir (7)

$$R = 5.85 \cdot 10^{-5} \alpha P_{\mu} \sqrt{\frac{M}{T}}$$

where P_{μ} is the vapour pressure in 1×10^{-3} Torr at $T^{\circ}\text{K}$ and M a mol of the substance being evaporated. Metals are generally monatomic in the vapour phase. The condensation coefficient α has been found to be equal to unity for most metals.

As the above consideration is applied to a phenomenon taking place in vacuo, in order to better define the used term "evaporation" the kinetic theory of gases can be used for calculating the fraction of the molecules emitted from the source which traverse a distance l without suffering a collision. That is because sometimes it is stated that for deposition of coatings by the evaporation process, the mean free path of the evaporating atom should be large compared with the source to substrate distance. From such calculations one could infer that a vacuum of the order of 10^{-4} Torr is adequate for most evaporations. However, it is an observed phenomenon that in most cases vacuo of the order of $10^{-5} - 10^{-6}$ Torr are necessary, and moreover that these values should be reached in as short a time as possible, i.e. of the order of a few minutes. The reason for these requirements on the vacuum is essentially the necessity of avoiding contamination of the substrate by residual gas in the vacuum chamber. Such contamination can arise even if the distance between the source and the substrate is sufficiently small and the gas pressure is sufficiently low so that collisions between molecules in transit can be neglected (14). The worst contamination by residual gas is caused by oxygen. It is found that the rate of deposition of oxygen atoms at

pressures above 10^{-5} Torr and at room temperature is of the same order as that of the condensing material under the usual evaporation conditions. In order to deposit a thin coating by this process, which would be free of contamination, except the interference coming from the residual gas, other sources of possible contamination must be considered. Such sources are the evaporant itself, the heater and also the substrate, i.e. the material to be coated. Proper preparation and selection of these is a vital step before starting the actual deposition of a coating.

The preparation of the evaporant is quite simple because the only requirements are a high degree of purity of the material to be evaporated and normal precautions in keeping both the material and the heater as clean as possible.

The geometry of the source varies widely according to the different requirements. For instance, an approximate "point source" is easily obtained by wrapping a wire of the substance to be evaporated around a V-shaped filament. The filament is resistively heated by passing a large current through it. If on melting the evaporant "wets" the filament it is securely held during the whole evaporation stage. On the other hand, when it is necessary to deposit a film over the internal surface of spherical holder, then a metal foil heater, e.g. that of "Knudsen type" is the appropriate one.

The preparation of the substrate is a much more complicated matter. Lapping and polishing may be the first step followed by careful degreasing, which is possible in an ultrasonic bath.

Sometimes etching is necessary to create clean and chemically active surfaces on which the coating will be deposited with good adhesion.

Another effective way of removing contaminating films from metal surfaces is by the action of ion bombardment in a glow discharge. In this case the metal surface is made a cathode electrode and the ion bombardment can remove absorbed gas layers as well as surface oxides if the discharge is in an inert gas or hydrogen. As Holland ⁽⁷⁾ reports there is a possibility of creating by sputtering a clean metal surface which could not be prepared by heat treatment in vacuo or in hydrogen. Ion bombardment cleaning of insulator surfaces is also possible in the positive column of a glow discharge.

The stage of preparation is followed by the stage of deposition. Once a suitable vacuum has been obtained, the evaporant is heated to start the deposition. This is done by electrical power (of the order of 100 - 1000 watts⁽¹⁴⁾ depending upon the boiling point of the source material). Most of this energy is dissipated as radiation, rather than in supplying the latent heat of evaporation to the metal, because the thermal exchange between heater and evaporant is poor. A more efficient system of heating the evaporant is, for instance, by electron bombardment. With this method the electron beam, usually accelerated by a voltage of several kV, produces the highest temperature in the vapour emitting surface and not in the evaporant support material.

The structure of the films obtained by this method, and thus their properties depend on the experimental variables during deposition.

Already, above has described the influence of the nature and pressure of the residual gases in the chamber. Some others are given below :

Substrate temperature and vapour intensity. There is a close relation between the substrate temperature and the condensation of the arriving atoms of the evaporant. This temperature should be below a critical value in order to start the condensation of vapours, otherwise they re-evaporate. The critical temperature increases as the intensity of the vapour stream impinging on the target surface increases. Langmuir, who established this, is speaking about condensation and re-evaporation, i.e. the incident vapour atoms linger on the receiving surface for a finite period.

According to this theory, as Holland⁽⁷⁾ cites, that a vapour atom has an average life on the surface on which it impinges before it re-evaporates. The average life of the vapour atom will be longer and condensation more likely, the more intense are the forces binding the atom to the substrate at the lower the substrate temperature. Thus, if the average life of a condensed atom is sufficiently long for another atom to collide with it before it re-evaporates, then an atom pair will be formed and the energy required to evaporate either of the atoms is considerably increased.

Thus, the greater number of vapour atoms reaching the substrate in a given interval of time the greater will be the possibility of nuclei being formed, either by vapour atoms directly impinging onto previously condensed atoms or by collisions between vapour atoms migrating on the substrate.

Effect of nature of the coating and substrate material. The structure of the coatings deposited onto a solid may be stable in the form of monolayers or agglomerates of atoms. During the condensation of atoms on a substrate they can be either uniformly dispersed or gathered up into a globule or agglomerate of small surface. If L is the latent heat of evaporation of a metal atom from the coated surface and L_{metal} the latent heat of evaporation from the native metal, then if $L < L_{\text{metal}}$ agglomeration is possible and if $L > L_{\text{metal}}$ the dispersed form prevails. Whether or not agglomeration can take place depends upon the mobility of the atoms on the substrate. The mobility of these atoms on the surface depends on the surface temperature which is far below the temperature needed to evaporate the atoms from the surface. There is also a correlation of the size and orientation of the crystals in evaporated metal deposits with their melting points. Films formed from high melting point metals consist of micro-crystals with no specific orientation, whilst films of low melting points metals produce large crystals showing definite orientation with respect to the substrate.

Effect of rate of evaporation. When a coating is deposited on a substrate it is found that the tendency to form agglomerates decreases as the rate of deposition is increased. At a high rate of film formation more nuclei are initially formed from which a fine grain deposit grows. The effect of rapid film formation enhances the hardness and wear resistance of thin films. This is attributed to the rate of deposition which is proportional to the rate of evaporation and not to the velocity with which the vapour atoms collided with the substrate.

Effect of contamination from the source material upon the coating structure and properties. The metals used for filament or foil heaters are those which combine the properties of high melting point and low volatility. They are in decreasing order of their melting points, tungsten, tantalum, molybdenum, niobium, platinum, iron, nickel and chromel. Of this group the most commonly used are tungsten and molybdenum. However, although the refractory metals have the forementioned properties, the evaporated films contain traces of the source material which has volatilized during film deposition. This contamination being evident in the effect it has on the structure and properties of the film. The extent to which the film is contaminated depends upon the respective volatilities of the evaporant and source material and the area of heater material exposed to the condensing surface. Chemical reactions between an evaporant and the source material may also give rise to volatile products.

1.2.2 Cathodic Sputtering

When an electrical discharge is passed between electrodes at a low gas pressure the cathode electrode is slowly disintegrated under the bombardment of the ionized gas molecules. This phenomenon is termed cathodic sputtering. The disintegrated material leaves the electrode surface either as free atoms or in chemical combination with the residual gas molecules. Some of the liberated atoms are condensed on surfaces surrounding the cathode whilst the remainder are returned to the cathode by collision with gas molecules⁽⁷⁾.

As in other vacuum-deposition methods, sputtering involves the

transporting of a material from a source to the part to be coated through the vapour phase.

In the simplest sputtering configuration the coating material (target) acting as the cathode and the part to be coated (substrate) placed on or near the substrate holder acting as an anode are held in a vacuum chamber and connected to a source of high voltage. The chamber is first evacuated and then back-filled with an inert gas, most commonly argon. The pressures used for the glow discharge during a sputtering procedure can be as low as 10^{-3} Torr. Below this pressure the discharge is usually extinguished⁽¹⁵⁾. Low pressures are required in sputtering applications to minimize collisions between sputtered atoms and gas phase impurities during the transport of material from the high-purity target to the substrate⁽¹⁶⁾. Through either Direct Current or Radio Frequency power supply, the target is given a negative bias, thus becoming a cold cathode electron emitter. Due to the existence of the electric field in the discharge, the electrons and the rest of the gas are in separate states, out of equilibrium. In particular, the energy gained by electrons may not be randomized collisions so that a Maxwellian distribution can be attributed to them⁽¹⁷⁾. The exact form of the electron energy distribution is still the subject of some controversy. The electron energy distribution is concentrated around a definite maximum value which depends on the field strength, gas pressure and collisional cross-section. This maximum value is very much greater than the applied field strength and the most striking non-equilibrium aspect of gas discharges is the disparity between the electron and gas temperature⁽¹⁸⁾. The electron temperatures are in the range of 10,000 - 50,000°K^{(10),(17)}. The gas temperature depends on

the pressure and at very low pressures this is not much above the ambient temperature⁽¹⁷⁾. Finally, the possibility of ionization and activation of gas molecules depend on the energy of the colliding electron.

Each gas has a certain threshold value of electron energy below of which only inelastic collisions occur. Above this value the probability of ionization on collisions increases rapidly to a maximum and then rather slowly falls away. So, the free electrons from the target (cathode) partly ionize the gas creating thus positive ions. These ions are accelerated towards the target and strike it with a high energy equal to, or less than, the voltage across the dark space depending on whether they collide with a gas atom during their traverse. A consequence of the ion impact on the cathode is first the emission of secondary electrons, which sustain the glow discharge and second the dislodging of an atom from the target (cathode) surface. These dislodged atoms move towards the part to be coated which is placed on or near the anodic parts striking it at such high energy that an atomic bond is created between the substrate and the coating⁽¹⁹⁾. This energy is varying in the region of $10^{(20)}$ up to 100 ev^{(6),(20)}.

The literature on cathodic sputtering is very voluminous and yet the knowledge of the mechanism by which metals and metal compounds are removed from the cathode surface is not clear. A number of different theories have been supported in different times but two of them are most widely accepted. These are the theories of "hot spot" and that of "momentum transfer". The former assumes that the atoms of the cathode are evaporated as ions due to the conversion of the momentum of the bombarding gas ions to heat at the surface of the cathode.

However, the momentum transfer theory seems to be better founded because of a number of different reasons. One of them is that in the case of thermally evaporated material the energy of the ejected particle is usually lying in the region of 0.1 - 1 ev^{(3),(4)} whereas with sputtered materials vary between 10 - 100 ev⁽²⁰⁾ as mentioned above. According to Carpenter⁽³⁾ the adhesion between coatings and substrates is a function of the acceleration and striking energy of the coating particles arriving at the substrate surface. In that case films deposited by the sputtering process would be expected to adhere better than the evaporated films; this is generally found to be the case. Thus, it would appear that the "momentum transfer" is more well established than that of the "hot spot" theory. Further support for this is the fact that the strong emission of electrons that would be expected to occur from "hot spots" has not been observed.

The outer surface of the cathode of a sputtering system, being exposed to the bombardment of charged particles and high velocity gas molecules which have gained thermal energy in the glow discharge, can have an appreciable rise in its temperature. As much as 50 per cent or more of the energy dissipated in the glow discharge appears at the cathode in the form of heat. Due to this the sputtering efficiency in terms of mass sputtered per watt-hour is increased. However, no critical vapourization temperature of the target material needs to be reached in the cases of sputtering in order to happen the transfer of coating material from target to the substrate. Thus even alloys and compounds can give coatings by sputtering without the undesirable fractionation of the constituent elements.

Coatings obtained by this process have very good adhesion in comparison to vacuum evaporation method. The reasons are, first the high kinetic energies imparted to the coating particles impinging on the surface to be coated⁽²¹⁾, the values of which are mentioned above and second the excellent cleaning of the substrate on an atomic scale which is kept clean during the coating cycle⁽²¹⁾. The sputtering process is theoretically a line of sight process⁽²⁰⁾. The particles of depositing material, except for some gas diffusion, follow optical lines and parts to be coated must usually be rotated or moved before the target. It should be pointed out that by proper positioning of parts sputtered films will, by gas diffusion, coat around corners. However, in achieving this phenomenon the depositing particles will strike the substrate surface with less energy than if actual line of sight impingement occurs. This affects the physical properties of the coating.

A range of different sputtering techniques⁽²²⁾ have been developed, i.e.

- Diode sputtering with D.C.
- Radio frequency sputtering (offering the ability to sputter non conductors).
- Triode sputtering with D.C.
- Sputtering with substrate biased.
- Sputtering with magnetic field included in the geometry.

The simplest of all these is the Diode sputtering with D.C. All that is needed is a cathode of the material to be sputtered, an anode and the substrate.

Practically all elemental materials, alloys and many compounds can be sputtered onto almost any substrate surface⁽²⁰⁾, but this sputtering technique cannot be used to deposit dielectrics. For this a Radio Frequency power source is used⁽¹⁹⁾. The reason for this is that in the case of R.F. sputtering the peak-to-peak voltage is usually of the range of 2kV and the net d.c. voltage across the dark space is below 1kV⁽²³⁾. In the case of d.c. sputtering, however, because of a much lower sputtering rate, it is necessary to use higher voltages, those of the range 2 - 4kV. This difference in the net d.c. voltage across the anode and cathode between the d.c. and R.F. sputtering creates film damage problems to the disadvantage of the d.c. sputtering. The film damage is most probably caused either by negative ion bombardment, or electron bombardment, or both, which in the case of d.c. sputtering have higher energies when they strike the substrate. This damage exhibits itself in various forms, such as high film leakage current, surface charge and even grain-texture film surfaces. The higher voltage is needed because of the low deposition rate in d.c. sputtering, due to the extremely low efficiency in the d.c. glow discharge.

R.F. sputtering is more advantageous than d.c. sputtering because of the higher rate of deposition, the absence of film damage and the improved chemical and physical properties of the created films. Another reason for using the R.F. technique in the case of insulators is that a d.c. accelerating potential cannot be directly applied to the cathode. Positive charges accumulated on the cathode surface during ion bombardment which slows down and ultimately prevents the

continuation of the sputtering. Using R.F. instead of d.c. potential, sputtering can be maintained on electrically non-conductive cathode materials. R.F. sputtering is also equally effective for both electrically conductive and non-conductive film deposition⁽²⁴⁾. Finally, although all metals can be deposited by cathode sputtering, the rates of deposition are slow in comparison to other methods, and vary between 100 and 1,000 Å/min^{(16),(24)}. This depends on the target materials, the applied voltage, the gas pressure, the distance between the target and substrate and the shielding of the target perimeter⁽¹⁶⁾. Due to low deposition rates this method provides an improved control of the film thickness.

Recently, another sputtering technique was developed called ~~plasma~~ atomic sputtering. This type of sputtering is done with an ordinary R.F. diode sputtering system, but the distance from target to the substrate is reduced to about 2cm. and the pressure increased by some 25 times⁽¹⁹⁾. These changes increase the number and energy of the ions striking the target, so that more atoms of target material are deposited in a given length of time. The process is claimed to give a better adherence and to be 2 to 3 times faster than the conventional sputtering process. Uniformity is said to be considerably improved.

The simplest sputtering system, as already has been mentioned, is the diode configuration, which uses a cathode and an anode. Reactive and bias sputtering are easily used in this configuration. Other more complex systems have been used. Triode and pentode configuration utilize additional electrodes as well as magnetic field plasma densification

to allow sputtering at lower pressures. The more complex configurations have their problems such as lack of versatility, complexity, non-uniform films, filament contamination and burn out, and problems in matching R.F. power to load. For these reasons, these configurations have been restricted primarily to the laboratory⁽¹⁹⁾.

1.2.2a Reactive Sputtering

Reactive sputtering can be defined as sputtering in the presence of a reactive gas so that the deposited film has a different chemical composition to the target material. The reactive gas can be a carbon containing gas, nitrogen or oxygen and the resulting coatings will be carbides, nitrides or oxides of the target metal.

Since all the metals of the fourth to sixth groups can be sputtered, an almost unlimited number of binary, ternary, or higher-order carbides and nitrides can be deposited by reactive sputtering. It is also possible to vary the non-metal-to-metal ratio by varying the partial pressure of the reactive gas. The number of oxides that can be produced by this technique are numerous⁽⁷⁾. Most reactive sputtering studies on the refractory compounds use the d.c. glow discharge technique (cathode sputtering) in which the discharge is established in an argon plus the reactive gas between the cathode and anode. The gas ions are accelerated to the cathode where they eject or sputter away the cathode material. The sputtered material is deposited on a suitably placed substrate.

Holland⁽⁷⁾ gives an excellent description of reactive sputtering and discusses in detail the possible mechanisms occurring during the

process of formation of metal oxide coatings. Many other investigators have produced theories on the physical processes taking place and it is generally agreed that there are three possible mechanisms by which a metal compound can be formed when sputtering is done in an active gas atmosphere :

- i) The direct sputtering in molecular form of the compound initially formed on the target surface by active gas ion bombardment.
- ii) The formation of the metal compound during transit of the sputtered metal to the receiver by collisions between active gas molecules and metal atoms.
- iii) Absorption of active gas molecules striking metal atoms during condensation at the receiver.

Little has been done, however, in determining which of the above mechanisms is operating. Toth⁽²⁵⁾ claims that during the formation of carbides or nitrides the reaction of the metal atoms with carbon or nitrogen probably occurs at the substrate. Putner and Jackson⁽¹⁵⁾ report that the first mechanism is predominant.

Although a glow discharge may be sustained with reactive gas only, it is considered that the use of a mixture of reactive and inert gas is indispensable for obtaining coatings of desirable properties. An explanation for this is the following :

- a) The ionized active gas molecules mainly combine with the target metal to form the metal compound.
- b) The ionized inert gas molecules utilise their energy in eroding the target substrate.

Thus the loss in oxygen ions in the formation of oxide on the target is reduced by using a high proportion of inert gas ions which do most of the sputtering.

It has been reported that the film properties of metal oxide coating are dependent on the composition of the gas atmosphere and therefore very close control of the composition of the gas components in the mixture is important.

Concerning the application of this method to refractory compounds like carbide, nitride coatings, it has not the same extent as with those of oxide coatings and is restricted mainly to binary compounds. Nevertheless, the ease of preparation, the high quality of the resultant coatings and the ease of composition control indicate that this method is superior in several ways to competing methods like, for example, reactive evaporation.

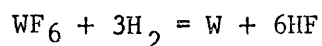
1.2.3 Chemical Vapour Deposition

In chemical vapour deposition a heated substrate is exposed to a mixture of gaseous reactants so that they interact to form a solid deposit on its surface. The gaseous reactants are metered, mixed and passed into the reaction vessel at a specific pressure which depends on their volatility and their stability on heating. The specimen is heated either directly by radio frequency induction heating or indirectly by placing the reaction vessel in a furnace. The first method has the advantage that the substrate is the only hot object within the whole apparatus. The gas mixture does not react until it reaches the heated surface and even then the reaction only occurs

directly at the surface so that a coherent continuous layer of material is built up on the specimen. The rate of flow through the reaction vessel is usually low so that streamlining effects are not serious. Consequently a coating of uniform thickness can be obtained over an object of complex shape. The transport of the reactant vapours into the reaction vessel is done by a carrier gas. In many cases a reactive gas such as hydrogen or oxygen is added to achieve either metal or oxide deposition. Compounds like carbides, borides and nitrides are deposited by using methane, boron trichloride and ammonia respectively⁽²⁶⁾.

The chemical reaction which deposits the coating must be chosen very carefully. The reactants must be volatile or gases so that they can be mixed and passed into the reaction vessel and must not decompose before reaching the reaction zone. The reaction must be activated by the temperature of the heated specimen. The temperature to which the substrate must be heated is dictated by the thermodynamic equilibrium of the chemical vapour deposition reaction and the kinetics of the reaction.

The reaction must proceed to give a coherent crystalline growth on the surface of the specimen and not a powder by reacting just above it. A typical chemical vapour deposition reaction is the reduction of tungsten hexafluoride by hydrogen, giving a coating of metallic tungsten.



Volatile compounds which are used in chemical vapour deposition reactions are listed on Table 2⁽¹³⁾.

TiCl_4 (136)	VCl_4 (149)		
TiBr_4 (230)			
ZrCl_4 (sub. 331)	NbCl_5 (254)	MoCl_5 (268)	
		MoOCl_4	
		Mo(CO)_6 (156)	
HfCl_4 (sub. 319)	TaCl_5 (242)	WF_6 (18)	ReF_6 (48)
	TaBr_5 (349)	WCl_6 (347)	ReCl_6 (> 550)
		W(CO)_6 (175)	

(Figures in parantheses are boiling points in °C)

TABLE 2 - Volatile Refractory Metal Compounds used in Chemical Vapour Deposition

Temperatures commonly employed for chemical vapour deposition are classified as: low 400 - 800°C for tungsten, molybdenum, medium 900 - 1,200°C for tantalum, titanium carbide and high 1,730 - 2,530°C for tantalum carbide, etc.

Examining the process itself, two basic factors should be taken into account. The first is the reactor geometry and the second the kinetics of deposition. The reactor geometry should be such, that

- i) maintain a constant transport of the vapours
- ii) avoid condensation losses on the cooler parts of the tube
- iii) take into account the opposite effects of gravity and natural convection

The kinetics of deposition should be such that a high growth rate and good quality coating is achieved. Parameters governing the kinetics of deposition basically are: substrate temperature, reactor pressure, flow rate and component partial pressures.

From the point of view of the coatings obtained, factors such as structure, thickness and adhesion with the substrate are the most important to be examined.

The structure of deposits is closely related to the rate determining step of the reaction. For choosing the conditions which will give the desired structure with a good reproducibility, informations should be taken from the kinetic investigation.

In saturation conditions the growth rate is high. Nuclei have no time for re-arrangement. The deposit is fine grained and the

crystallites are oriented at random. Below saturation, the whole process is diffusion controlled. This means that gaseous molecules impinge on the substrate from time to time, the growth rate is low and re-arrangement on the substrate surface is possible. These conditions yield large, oriented crystallites⁽²⁶⁾.

The influence of foreign gases is worth noting because it can affect the structure of the deposits and also the whole mechanism of deposition.

The thickness provided by this method sometimes can be as much as several millimetres but generally such a large value is not necessary to achieve the required mechanical properties. So coatings of the range of one hundred microns are sufficient. More often a limitation occurs when the crystallites grow larger and larger providing coarseness and lack of cohesion. For example, metallic coatings of rhenium and tungsten can be built up to a thickness of several millimetres but brittle coatings of titanium carbide and zirconium carbide can only be obtained by layers of a few micrometres thick. The deposition rate varies from 300 μm per hour for tungsten to 5 μm per hour for titanium carbonitride.⁽¹³⁾

Concerning the adhesion which is given by this method it is said to be good because a significant amount of diffusion occurs across the coating substrate interface. For example, titanium carbide deposited on steel at 1,000°C shows diffusion up to about 5 μm ⁽¹³⁾.

Finally, a very significant feature of all chemical vapour deposition coatings is their high density and freedom from voids.

With this method it is possible to coat relatively complex geometric surfaces and the coating obtained is a uniform one, because the mixture of gaseous reactants is homogenously surrounding the uniformly heated substrate of the substrate. This is the result of diffusion of gases which, according to Viguie⁽²⁶⁾ multiplies ten fold when the temperature is increased from room temperature to 1,000°C. So, due to these reasons the chemical reaction which takes place proceeds with the same speeds towards the whole direction of the heated substrate.

1.3 Plating of Different Substrates with Titanium Carbide by Different Vapour Deposition Processes.

Titanium carbide is a refractory material which exhibits a wide range of beneficial properties to problems related with friction and wear resistance. This is due to its high hardness and resistance to wear. At the same time other properties like its inertness to the most common chemical reagents (acids and alkalis)⁽²⁷⁾, its resistance to corrosion by some molten metals⁽²⁸⁾ and finally its high melting point makes it attractive for many applications connected with the improvement of surface layers of different substrates. In this case the titanium carbide is applied on the substrate in the form of a coating. Substrates which usually are coated with titanium carbide are steel (common⁽²⁸⁾ or pretreated⁽²⁹⁾) or cemented carbides⁽³⁰⁾,⁽³¹⁾,⁽³²⁾ or even refractory metals⁽³³⁾,⁽³⁴⁾. Methods which have been used for the application of the coating on the substrate cover most of the range of physical vapour deposition methods. Due to its simplicity regarding the needed equipment, many investigations have been carried out using the chemical vapour deposition process⁽²⁸⁾,⁽³²⁾,⁽³⁵⁾,⁽³⁶⁾. Recently, coating by the sputtering process⁽²⁹⁾,⁽³⁷⁾ has been reported and since advanced high power density heat sources such as electron beam guns have been available, methods like reactive ion plating⁽⁸⁾ and activated reactive evaporation⁽³⁴⁾,⁽³⁸⁾,⁽³⁹⁾ have been used for the same purpose.

Examination of these methods show that only the chemical vapour deposition technique utilizes gas phase reactants, because in the case of sputtering there is the transport mechanism of titanium carbide particles from the target to the substrate and in the case of reactive ion plating titanium atoms are ejected into the reaction region from a

solid titanium source by evaporation with the use of an electron beam gun.

In the chemical vapour deposition method one of the reagents is titanium containing vapour which comes from a volatile compound of titanium. However, the volatile compounds of titanium are very few. Titanium tetrachloride and titanium tetrabromide are the most readily available. As it can be seen from Table 2⁽¹³⁾ the boiling point of the first one is much lower, 136°C, than that of the second, 230°C, so most of the investigations have used titanium tetrachloride. Another volatile compound of titanium which is readily available is the organometallic compound tetra-isopropoxy titanium (b.p. 230°C).

Titanium tetrachloride is introduced into the reactor with the use of a carrier gas which is usually hydrogen or an inert gas by bubbling it through the liquid reagent. The concentration of titanium tetrachloride vapour is controlled by varying the temperature of its heating bath.

Concerning the second reagent, which is the carbon containing species, there is a variety of choice from the whole class of hydrocarbons, i.e. aliphatic, the saturated paraffin series, such as methane^{(31),(32),(36),(40)} and propane^{(40),(41)} or the unsaturated hydrocarbons such as ethylene⁽⁴¹⁾ and acetylene or even from the aromatic series such as benzene⁽²⁸⁾ and toluene⁽³²⁾. Another commonly used carbon source is carbon tetrachloride^{(42),(43)}.

The experimental parameters affecting the rate of growth and at

the same time the quality of the deposited materials are as follows:-

- Substrate temperature
- Pressure of the reaction chamber
- Gas flow
- Ratio of the reactants used

The temperature of the substrate is determined by the thermodynamics of the reaction of titanium tetrachloride with the hydrocarbon used⁽¹³⁾.

The energy required to heat the sample and to maintain it at the proper temperature, where the reaction is taking place, is provided either by radio-frequency induction methods^{(32),(40)} or tubular furnaces^{(28),(41)}. Generally the temperatures required are of the range 900° - 1200°C.

Pressures used during a coating experiment are approximately atmospheric. The gas flow is varied according to the capacity of the reactor and also according to the required deposition rate⁽³²⁾. Finally, the ratio of the reactants used is varied according to the desired composition of coatings.

The growth morphology of the coating is very strongly dependent upon the surface state of the specimen and also its temperature. According to Lee and Richman⁽³²⁾ when the coating temperature and the hydrocarbon concentration in the reactant gas mixture are relatively low, whiskers often form. At an intermediate temperature and with a moderate concentration of hydrocarbon, large well-defined crystal growth is seen. Finally, at high temperature, i.e. at the upper edge of the kinetic-controlled region, a coarse polycrystalline film is formed. Therefore, by choosing carefully the experimental conditions it is possible to obtain the coating structure desired. Thus it can be said that the preparation by chemical vapour deposition

of dense, porosity free coatings does not present any particular difficulty. On the contrary satisfactory adherence of the deposit on steel substrates is much more difficult by this method. This lack of adherence can be attributed to a number of different reasons, such as:-

- The considerable difference between coefficient of linear thermal expansion of titanium carbide ($7.6 \times 10^{-6} \text{C}^{-1}$)⁽³⁰⁾ and that of steel ($11.7 \times 10^{-6} \text{C}^{-1}$)⁽⁴⁴⁾. This particular problem is eased using the cemented carbide substrate of which the corresponding coefficient is more or less the same ($6.5 - 7 \times 10^{-6} \text{C}^{-1}$)⁽³⁰⁾, as that of titanium carbide.
- The formation in the interface between deposit and substrate of an intermetallic brittle zone, which is more pronounced when cemented carbide is used as substrate. In this last case the intermetallic component is $\text{Co}_6\text{W}_6\text{C}$ (eta-carbide). It was generally believed that the existence of this compound was detrimental to the adherence due to its brittleness but Sproul and Richman⁽³⁷⁾ with their investigation have suggested that the opposite is true.
- The existence on the substrate surface of an oxide film causes a further harmful effect on the adherence of the coating⁽⁴⁵⁾.
- Finally, an attack of the substrate by the halide formed before the main deposition process occurs, contaminates the substrate surface.

For overcoming inherent problems of bad adhesion different precautions were taken prior to the actual deposition of the coating. However, sometimes after the coating has been deposited in order to improve the bond between the coating and the substrate the samples are subjected to diffusional annealing in a hydrogen atmosphere at relatively high temperatures and for prolonged periods⁽²⁸⁾.

The coatings obtained are of high purity providing that the reagents used are themselves of high purity and that the reactor has been thoroughly flushed for the removal of oxygen before the coating procedure starts.

In the case of titanium carbide coatings produced by sputtering, the substrate is mounted on an anodic part of a sputtering system. At the same time the titanium carbide target is mounted on the cathode of the system. The whole coating procedure takes place in an inert gas atmosphere and usually this is argon. After the system is evacuated to pressures 1×10^{-6} Torr by the use of proper pumping units, in order to remove the residual gases, then the system is back filled with high purity argon to a pressure where a glow discharge is sustained. This pressure is usually of the range 1×10^{-3} - 5×10^{-2} Torr. By activating the glow discharge then the substrate is etch-sputtered for a time up to half-an-hour before being coated to ensure a clean substrate surface. After this stage the actual deposition period begins and it is extended up to the point that the desirable coating thickness is obtained. The experimental parameters affecting the rate of deposition, the coating morphology and its structure are as follows:-

- Argon pressure
- Distance between target and substrate.

- Target and substrate temperature
- Applied potential between the electrodes and
- Intensity or current density of the electric discharge.

The residual pressure of argon is restricted within the limits, where the glow discharge is self-sustaining. The pressure of argon also plays an important role in the adhesion of the coating to the substrate and according to Mukherjee et al⁽²⁹⁾ the adhesion shows a very strong inverse relation to pressure.

The distance between target and substrate is a vital factor for the thickness of the coating because according to cosine law⁽⁷⁾, the thickness of the coating is inversely proportional to the square of the target-substrate distance.

The target and substrate temperature contribute to the method in different ways. By increasing the target temperature the ejection of cathodic material is increased. Increase of the substrate temperature helps the diffusion of the coating material in the surface layer of the substrate, due to the increase of surface and bulk mobilities of deposited atoms⁽²⁹⁾. The applied potential provides the kinetic energy of the ions bombarding the substrate. The potential used is usually 1,000 - 4,000 volts. Mukherjee et al, using a negative D.C. bias to the substrate during the initial stages of an rf sputtering deposition, have found that adhesion is increased due to the higher penetration of energetic ions and neutral atoms into the steel lattice. They have found that an interfacial region of about 0.5 μ m exists between steel substrate and titanium carbide coating and which has a titanium concentration well above its room-temperature solid solubility in iron, approximately 2%, and so they conclude that the mixing of titanium is a result of non-diffusive processes.

Finally, it should be mentioned that no details are given by the above mentioned investigators of the influence of the current density or current on the nature of the coatings during the deposition.

Sproul and Richman⁽³⁷⁾ investigating the influence of the intermediate eta-carbide layer, which forms during the chemical vapour deposition process between cemented carbides substrates and titanium carbide coatings, have used a sputtering method to produce their coatings. The sputtering system was operating with an rf arrangement in an argon atmosphere of about 5×10^{-3} Torr. They used two targets; the first was a specifically prepared eta-carbide made by sintering and the second was titanium carbide commercially available. Eta-carbide deposition was followed by deposition with titanium carbide, with this arrangement they produced titanium carbide coatings with or without the eta-carbide layer. The sputtered eta-carbide ($\text{Co}_6\text{W}_6\text{C}$) coatings were amorphous and the bonding between them and the substrate was poor. The coating could be scratched and removed easily with a knife. The titanium carbide deposited on this surface was always amorphous. When the carbide was coated directly on the substrate without the interposition of the eta-carbide layer it was either amorphous or crystalline depending upon the substrate temperature. Bonding between coatings and substrate was also poor and it could also be scratched and removed with a steel knife. In order to improve the bonding of the coating the specimens were heat treated at 700°C for one hour in the presence of hydrogen. With this treatment the amorphous coatings become crystalline.

The deposition rate of titanium carbide is low as always happens with the sputtering technique and was of the order of $950 \text{ \AA} \cdot \text{hr}^{-1}$

In the case of "titanium carbide" coatings produced by the reactive ion-plating process the substrate is the cathode of the system exposed to ion bombardment during the whole deposition procedure. In this process metal evaporated from a source, reacts with an atmosphere of reactive gases, giving a coating on the substrate. Stowell⁽⁸⁾ using this method prepared a fine mixture of titanium and carbon co-deposited on a mild steel substrate. The source used was an electron beam gun with a magnetically deflected electron beam through an angle of 270° . The electrons are electrically accelerated through a potential of 10 kV to provide energy to heat the source for evaporation. This was a standard 1 in. rod fed titanium source. To prevent rapid degradation of the electron-emitting filament, it was separated from the deposition portion of the coating unit by a flow-limiting baffle. This baffle arrangement made it possible to maintain pressures of less than 1×10^{-3} Torr in the vicinity of the filament, while pressures in the deposition section of the coater were as high as 60×10^{-3} Torr. The reactive gas used was ethylene.

The deposition parameters upon which the composition of coatings were dependent are gas pressure, substrate voltage and evaporation rate, while the distance between evaporation source and substrate was kept constant 14 cm. By changing one or more of these parameters the stoichiometry of the reaction was controlled. The reaction taking place happens in the gas phase before the material deposits, or it can happen on the substrate.

The gas pressures used varied between 12×10^{-3} Torr and

60×10^{-3} Torr while the voltages were lying in the region of 2 to 5 kV. At low pressures the deposition of carbon into the film was slow and at high pressures heavy depositions of carbon occurred. The same behaviour of carbon deposition is displayed by varying the substrate voltage. The deposition rates achieved by this method were ranged from $5 \mu\text{m} \cdot \text{min}^{-1}$ up to $15 \mu\text{m} \cdot \text{min}^{-1}$, which are exceptionally high in comparison to other methods already mentioned, but the basic disadvantage is that the coatings obtained were not chemically reacted but were a fine mixture of titanium and carbon co-deposited particles.

The coatings produced were very ductile and had very low hardness. To cause compound formation several heat treatments were performed. The temperatures used were between 950°C - $1,050^{\circ}\text{C}$ and time varied from one to five hours. With such a heat treatment, a precipitation of particles occurred within the film and a continuous hard layer began to form along the outer edge. These particles are considered to be titanium carbide of relatively high hardness dispersed in a low hardness matrix, though no analytical details are given by the author⁽⁸⁾. So the method described produced a coating which could not be described as titanium carbide and even after heat treatment such a coating is not obtained.

In the case of activated reactive evaporation which has been widely reported by Bunshah and co-workers^{(34), (38), (39)} it can be said that this method is similar to reactive ion plating, which has been described above, from the aspect of introduction of reactive species into the chamber. It differs, however, in respect of the mode of activation of the reacting species and also that the titanium

carbide is deposited onto an independently heated substrate, the temperature of which is not a limiting factor for the start of the reaction as may be the case in reactive ion plating. Basically this method is a reactive evaporation method which utilizes activated species of metal vapour and hydrocarbon gas atoms in the vapour phase in a reaction zone, i.e. in the space between the substrate and the metal source. The source metal, titanium, is heated and vapourized in the vacuum chamber by an electron beam gun to provide the metal vapour atoms in the reaction zone. The hydrocarbon gas, acetylene, is introduced into the chamber where it and the metal vapour is activated by some of the electrons of the metal heating electron beam. These are deflected into the reaction zone by a low voltage field, produced by a positively charged electrode. Acetylene was chosen because it is a highly unsaturated hydrocarbon, while methane was not considered a suitable gas due to the saturated carbon-hydrogen bond. The activated reactants increase the probability of a reaction between them, and the metal vapour-hydrocarbon gas reaction is achieved with a high efficiency, producing the desired metal carbide film on the substrate. With this process, deposition rates are substantially higher than those achieved by the other methods already described ranging from $1 - 12 \mu\text{m} \cdot \text{min}^{-1}$ (39). Only reactive ion plating provides deposition rates comparable to activated reactive evaporation. The reaction between the metal vapour atoms and gas atoms takes place in the zone between the metal source and the substrate. The formed titanium carbide is deposited on resistance heated tantalum substrates, in the temperature range $520 - 1,450^{\circ}\text{C}$. This method has two independently controlled steps, i.e. first the synthesis of the depositing species and second the film growth. The substrate temperature is not a limiting factor for the formation of the carbide but it influences the properties

of the formed coating, because the microstructure of the deposit is dependent on the substrate temperature which can be varied at will. Hence the properties of the deposit can be controlled. The stoichiometry of the compound can be varied by changing the ratio of the reactant species supplied. For temperatures in the range 0°C to about $0.3T_m$ (T_m being the melting point of the compound in degrees Kelvin), the deposit is of less than full density, though the density increases with deposition temperature. The morphology exhibited by the deposit is of tapered crystallinities with porosity in between the crystallites. Such deposits showed microhardness values of about $3,000 \text{ kg.mm}^{-2}$. At substrate temperatures greater than approximately $0.3T_m$ the deposit becomes fully dense and its morphology shows columnar grains across the thickness of the deposit. Such a structure contains fewer imperfections (i.e. porosity, cracks, etc.) and hence exhibits much higher Knoop microhardness value $4,000$ to $5,000 \text{ kg.mm}^{-2}$. Summarizing, it can be said that the operational parameters used in this method are as follows: gas pressure, substrate temperature, evaporation rate, gas flow, activating probe voltage, and distance between metal and substrate. However, for reasons of easy control of the method, all are kept constant and only substrate temperature and gas flow varied. The values of other parameters are pressure 5×10^{-4} Torr, evaporation rate 0.66 gr/min. , activating probe voltage $100 - 250$ volts and distance between metal and substrate 15 cm.

Finally, a method should be mentioned that is somewhat different. Though gas phase reactants are used as in C.V.D., the source of activating energy is different. This method is described by Elyutin et al⁽³³⁾ who report that the energy required to maintain the carbide forming reaction and heat the surface of the substrate is

supplied by an impulse created plasma. The titanium carbide coatings are produced from vapour phases containing hydrogen, titanium tetrachloride, methane or acetylene. The substrates used are tungsten, molybdenum and graphite. They have examined the effect of the partial pressure of the titanium tetrachloride in the gas flow ($H_2 + 20\%CH_4$ by volume) on the growth of the carbide coating thickness produced by a constant number of plasma pulses (5,000) and they found that the thickness increases with increase in titanium tetrachloride partial pressure up to approximately 6 Torr. Any further increase in titanium tetrachloride partial pressure has practically no effect on increase in coating layer thickness which becomes constant at approximately $15\mu m$. All subsequent precipitation experiments were carried out with a titanium tetrachloride partial pressure of 6.5 Torr. The behaviour of the process was studied in relation to the number of impulses fed to the plasma (time) and methane content of the vapour gaseous phase. The results of these experiments show that the thickness increases as a function of pulse number and concentration of methane, although the effect of this factor becomes negligible at high methane content (30 and 50%). Experiments involving replacement of the methane by acetylene show that the latter produces a much greater acceleration of the carbide formation process than methane. Experiments carried out for depositing titanium carbide on different substrates show that the titanium carbide layer growth rates on tungsten and molybdenum substrates are almost identical. The titanium carbide deposition rate is slightly higher on graphite, this possibly being due to participation of the carbon of the substrate in the carbide formation process. The relationship between the microhardness of the coatings produced on tungsten and molybdenum substrates and the number of impulses show that microhardness is higher for greater pulse number and that it is higher for coatings

on tungsten than on molybdenum. This difference in microhardness of the titanium carbides on the tungsten and molybdenum is ascribed to the effect of the substrate material. (Hardness, 520 kg.mm^{-2} for the tungsten and 240 kg.mm^{-2} for the molybdenum). Finally, they have found that the microhardness of the titanium carbide layers produced, also depend on the composition of the gaseous mixture from which the deposition is carried out and it is shown that the microhardness is higher at higher compositions of methane.

CHAPTER 2

ELECTRICAL BREAKDOWN IN GASES

2.1 Introduction

Gases are normally good electrical insulators and find extensive application as such. However, application of an electrical field of sufficient strength can lead to gas breakdown, ionization and electrical conduction, with the appearance of a luminous electrical discharge. Variation of the voltage or the operating pressure leads to an alteration in the nature of the discharge. Transition from the insulating to the conducting state occurs more or less gradually as the applied electrical field is steadily increased⁽¹⁸⁾.

An electrical discharge is created in a gas when a sufficient number of electrons are removed from the atoms to make the gas an electrical conductor. A discharge can be generated by a variety of methods, however by each method enough energy must be provided to ionize the gas. All electrical discharges are characterized by the presence of both free charges and an electric field. The free charges are primarily electrons and positive ions, although negative ions may also exist. Two of the most obvious examples of electrical discharges occurring the first in nature and the second artificially are: lightning and the luminous neon signs, respectively.

Generally, energy must be added to a gas to create the electric field and the charge carriers essential to any electrical discharge. Several methods are available to supply this energy. A direct, non-

electrical method of ionizing a gas such as argon utilizes radiation of wavelength corresponding to the ionization energy⁽¹⁶⁾. Radiant energy sources are impractical for sustained discharges and only electrical sources are useful to produce discharges for practical applications. However, these methods also cause changes in electron energy levels during excitation, ionization, or recombination in the gas. This gives rise to photon emission, which causes the luminous zones characteristic of most electrical discharges. This is always observed in the arcs and glow discharges. The colour of the discharge naturally depends on the energy levels and thus on particular gas involved. The electric field can be applied with either a dc or an ac source. The latter may or may not require internal electrodes. The mechanism of generation and the properties of the discharge are determined by the method used to supply the electrical energy.

2.2 General Consideration and Classification of Gas Discharges

There are several types of gas discharges. For chemical synthesis they can be conveniently classified into two main types: thermal discharges and non-thermal discharges. To be exact all the chemical activation in a discharge should be ascribed to thermal excitation of the electrons. However, while the electron temperature in a discharge is high, it is not necessary for the bulk temperature to be as high. Due to its very small mass, an electron passing through a potential drop of 1eV acquire very high kinetic energy which has an equivalent temperature of about 10^4 °K⁽¹⁶⁾. This energy is transferred to other particles in the plasma by collisions and therefore the entire gas can be heated. Although the amount of energy transferred during each collision is small, at relatively high pressures the frequency of collisions may be sufficient to distribute the thermal energy uniformly among the electrons, ions and un-ionized species.

High-pressure plasma, such as produced by arc plasma torches, are operating at approximately atmospheric pressure and can maintain temperatures from 5,000°K to 40,000°K for extended periods of time⁽¹⁶⁾. The high-pressure plasmas are usually referred to as thermal discharges. Because of the produced high temperatures, high-pressure plasmas are used for applications such as metal cutting, spray coating and ultrafine particle forming. On the other hand, for discharges in a pressure range below several Torr, the electron and ion temperatures can differ by several order of magnitude. A glow discharge used for applications of sputtering or ion plating is described as low-pressure plasmas and usually is referred as plasma of non-thermal discharge⁽¹⁶⁾. The gas

temperature is therefore one convenient criterion on which a classification of discharge can be based.

Another classification criterion is the magnitude of discharge current⁽¹⁷⁾. In this case the gas discharges are generally classified in three types, according to their current :-

- (a) The Townsend or dark discharge, which carries currents up to 10^{-6} A.
- (b) The glow discharge, which carries currents from 10^{-6} A to 10^{-1} A approximately.
- (c) The arc discharge, which carries currents of about 10^{-1} A upwards.

The Townsend discharge is created by photoemission and by photoionization, the glow discharge by positive ions bombardment of the cathode, and the arc discharge by thermionic or field emission from the cathode. The cathode may be heated by an external source or by the discharge itself.

During a gas discharge, alteration of the applied potential allows passage from one to the other class of discharges. In the case of discharges which strike between electrodes, the current follows the curve shown schematically in Fig. 1, as the voltage is increased. This curve defines the types of electrical discharges described above. In general the electric field strength and the pressure of the gas determine the type of discharge generated. At very low voltages the few free electrons and ions that exist in an ordinary gas under ambient conditions are accelerated to the electrodes, where they are neutralized to produce a small current. Eventually the current levels off, and the saturation value is limited by the number of charge carriers that can reach the electrodes. A further increase

in voltage gives to some electrons sufficient energy to ionize gas atoms, thereby generating additional charged particles. In addition to ionization, there is a current increase due to secondary electron emission from the cathode as it is bombarded with positive ions. The current increase leads to breakdown in the gas, as indicated in Fig. 1.

The Townsend discharge appears before breakdown and is characterized by very low currents, of the range of microamperes, and is invisible because the density of the excited atoms which emit the visible light is small. Because of this small density of the excited atoms Townsend discharge is not self-sustained and so requires external sources to produce electrons.

Following breakdown in the gas, on increasing the applied potential the secondary emission of electrons from the negative electrode is increased, and thus the electrons lost at the anode, or by recombination in the gas, can be replaced. This is the reason that the discharge becomes self-sustaining, and the sharp rise in current causes the transition to either a glow or arc discharge with the simultaneous luminous effects of the discharge gases. Such a transition from the glow discharge towards the arc discharge is depending on the gas used and circuit conditions⁽¹⁷⁾. In the case of the arc discharge the gas is intensively luminous and may give an impression of violent turbulence. A glow discharge usually is characterized by currents in the milliampere region at pressures of the range of millitorrs but it can be operated at a pressure as high as 760 Torr. In the latter case though, the current increases rapidly owing to heating of the cathode, and the glow discharge may transform

into an arc. In the arc discharge the current is very high and the voltage is low, as shown in Fig. 1.

Arcs operating at atmospheric pressure have very high temperatures. In a flowing gas or arc plasma torch, convection current distribute the heat content throughout the gas. In practice, the arc discharge can be generated without passing through the glow discharge region. In this case a transient spark gives rise to a stable arc.

Another type of electrical discharge is the corona, which is usually generated between cylindrical electrodes and differs from an ordinary glow discharge in that breakdown occurs in a non-uniform field. Current in the milliamperage range can be sustained.

Due to the fact that the glow discharge is involved in chemical ion plating (the technique used in the present work) a more extensive consideration of this is given below 2.3.

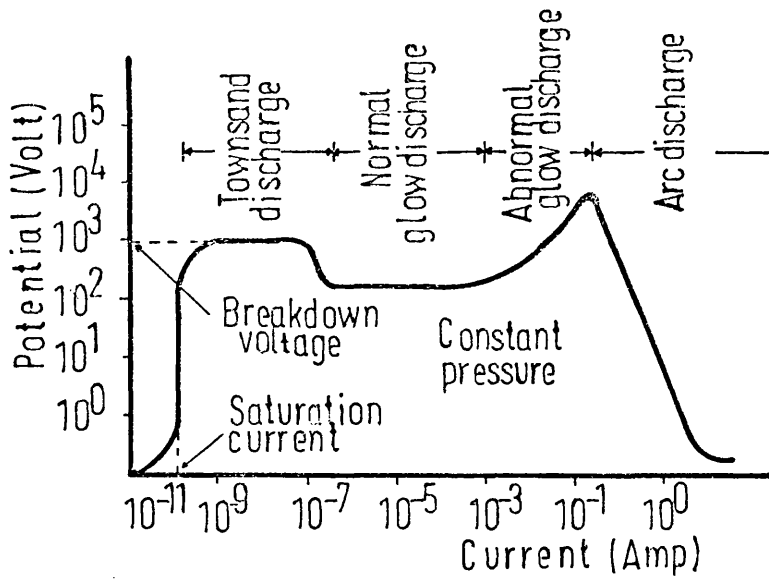


FIG.1. Typical Voltage-Current characteristics, for the d.c. discharge showing regions where the various types of discharge occur (after P.L. Spedding)

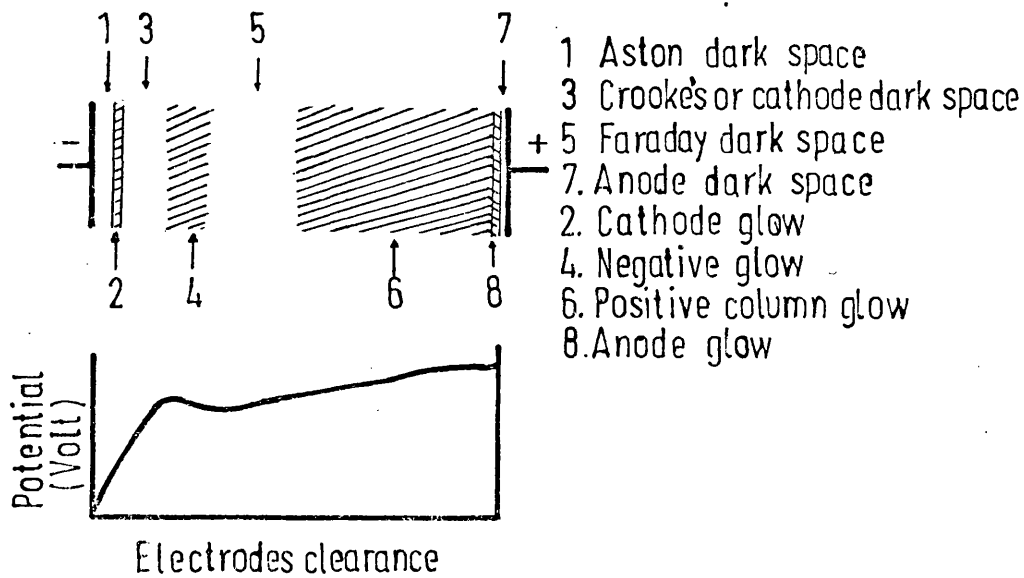


FIG.2. The distribution of dark and luminous zones in a low pressure d.c. discharge (after P.L. Spedding)

2.3 The Glow Discharge

The d.c. glow at low pressure is one of the most familiar gas discharges, largely because of the ease with which it can be produced and maintained, and because of its distinctive appearance which depends on the pressure used⁽¹⁷⁾. This pressure is usually a few Torr and the obtained discharge is a uniform glow throughout the tube or the reactor, providing the applied voltage is sufficiently high to cause the discharge to strike⁽⁷⁾. As the pressure is further reduced, generally under about 20×10^{-3} Torr⁽¹⁸⁾, the glow discharge is characterized by a series of discrete dark zones assuming the form shown in Fig. 2. In front of the cathode is a glow termed the cathode glow, followed by a dark space called the cathode or Crooke's dark space. The cathode dark space is followed by another glow called the negative glow, which is the most luminous of all the glows. This is followed by the Faraday dark space, and a long glowing region known as the positive column. Under some conditions an anode glow and anode dark space may surround the positive electrode. Also at low pressures it may be possible to discern a dark space known as the Aston dark space between the cathode and the cathode glow.

Further reduction in the gas pressure will cause the cathode dark space to expand at the expense of the positive column and when a pressure of the order of 10×10^{-3} Torr is reached the cathode dark space will be several centimetres in length. Should the cathode dark space expand sufficiently to contact the anode electrode the discharge is extinguished⁽⁷⁾. This is because the impedance of the glow discharge alters very little until the cathode dark space approaches the anode and when this happens the impedance rises rapidly as the cathode dark space starts to envelop

the anode. At this point the glow discharge disappears and only a very small current flows⁽¹⁵⁾. Conversely, as the operating pressure is raised, the positive column expands to practically fill the whole interelectrode space⁽¹⁸⁾.

The effect of changing pressure is pronounced and follows a simple law: The length of the cathode dark space is found to be inversely proportional to pressure. The lengths of the other regions vary in roughly the same way, except for the positive column, which continues to occupy as much of the tube or reactor length as is available to it. Extremes of pressure put approximate limits on the retention of the glow discharge characteristics. At very low pressures, when the cathode dark space fills the entire tube or reactor, the discharge is becoming more like an electron beam and beyond this, with pressures below 1×10^{-3} Torr or so, the supply of electrons by positive ion bombardment is no longer sufficient to maintain the current unless the applied voltage is very high⁽¹⁷⁾.

It should be noticed that at constant pressure, the interaction of the discharge regions depends on the tube or reactor geometry. In this case the size of the positive column contracts when the electrode spacing is reduced⁽¹⁸⁾.

In each of these regions various different chemical and physical phenomena are important. For example, the dark spaces can be conveniently viewed as regions in which charged particles are accelerating while the glowing regions are areas where impact ionization and excitation are taking place. The potential drop in the positive column is orders of magnitude smaller than in the other regions⁽¹⁸⁾,

and generally it can be said that most of the potential fall between the anode and the cathode occurs across the cathode dark space owing to the space charge of positive ions⁽⁴⁶⁾. The negative glow, Faraday dark space and positive column have a high conductivity, contain a high proportion of ionized gas atoms and this region is commonly referred to as the "plasma" in which electrons and positive ions are present in approximately the same number per cm³. Ions in the "plasma" region move around with a thermal motion, as defined by the classical gas kinetic theory. Any positive ion arriving at the dark space-negative glow boundary is affected by the strong electric field across the cathode dark space and is accelerated to the cathode, hitting it with an energy equal to, or less than, the voltage across the dark space, depending on whether or not it collides with a gas atom during its traverse. The impacting ions give rise to two major phenomena; sputtering of atoms and the release of secondary electrons. The electrons are accelerated across the dark space into the negative glow region and provide the necessary ionizing action to sustain the discharge⁽¹⁵⁾. So it can be said that in the glow discharge regions take place the transformation of the electrical energy into kinetic energy, mainly of electrons and in minor extend of the atoms present⁽⁴⁶⁾.

From all the above regions which are found in a glow discharge, it is necessary to study more extensively the cathode or Crooke's dark space because of its practical importance to the ion plating method. As can be seen in Chapter 3, the adhesion of coatings is mainly dependent upon the kinetic energy of the coating species (positive ions and energetic neutrals). This kinetic energy is a function of the cathode fall in this dark space. The cathode fall of potential is the

term applied to the difference of potential across the cathode dark space. If the electrodes are a short distance apart, this difference is almost equal to the full potential difference between cathode and anode. In the case of normal glow discharge the cathode fall is constant over a certain range of current values. This may be ascribed to the circumstance that, over the transitional range between Townsend and glow discharge region, the discharge gradually contracts in breadth. When the glow discharge just appears, only part of the cathode is covered with glow.

In the normal glow discharge the covered area steadily increases with the current, so that the current density; (current per cm^2) tends to remain constant. While this is happening, the voltage remains constant, and the current grows in direct proportion to the area of the negative glow. This is the region of the normal cathode fall (V_n). Any further increase in current increases the current density and the discharge is then described as abnormal glow discharge. In the region of the abnormal glow discharge, if the current is increased furthermore, the cathode fall of potential increases and becomes abnormal. The current density in that case increases, and thus also the space charge of positive ions, which causes a still greater concentration of the field at the cathode and compression of the Crooke's dark space. For these reasons the primary electrons from the cathode surface enter the negative glow space with greater velocities than in the case of normal glow discharge, and form a bigger percentage of ions there. As the percentage of ions formed increases, the border between glow and dark space becomes more sharply demarcated particularly in noble gases.

The normal cathode fall, V_n , has a characteristic value for each combination of gas and cathode material. Usually this value is only little dependent on the pressure of the gas. The V_n values given by Penning⁽⁴⁶⁾ for argon discharge and various cathode materials is as follows :-

Cathode	K	Mg	Al	Fe	Ni	Mo	Pt
Normal Cathode Fall (Volts)	64	119	100	165	181	103	131

As mentioned above, once the current has increased to the point where the whole cathode is covered by negative glow, the discharge enters to the abnormal glow region characterized by an abnormal fall of potential at the cathode. Here, then, the voltage across the dark space (V_a) is greater than V_n , and it continues to increase with increasing current. In general, V_a retains the same value when the current density j is made to vary inversely with the square of the gas concentration; V_a , therefore is a function of j/Po^2 . This is also the case when the cathode fall is normal. However, the V_a as a function of j/Po^2 for the same cathode material under the same gas discharge conditions may deviate from one run to another, the reason being, possibly, that gas and cathode are heated by the discharge, so that, consequently Po is not known exactly. Also, heating of the cathode per square centimetre of its surface depends on j and not on j/Po^2 , so that at a certain value of V_a , the temperature of the cathode depends directly on Po . Sufficiently heated, the cathode starts to emit electrons thermionically, as well as by ion bombardment. The abnormal glow discharge has important applications in fields related to ionic bombardment cleaning of substrates, cathodic sputtering, and ion plating.

Combining these theoretical details, it can be said that in practical applications as in sputtering and ion plating, the glow discharge is employed as a source of ions. These are generated in a low pressure environment by high speed electrons ionizing part of the different gas species in the working chamber⁽¹⁵⁾. The electrons are the essential constituents of the discharge as they are the agents which transmit the electrical energy from the power source to the gas⁽¹⁸⁾. The glow discharge will be self-sustaining provided sufficient electrons (primary and secondary) are emitted and introduced into the plasma to replace those lost by recombination, passage to the chamber walls and other processes. The glow discharge has a low pressure limit. At this limit the plasma's electron density becomes too low to be useful, or the replacement mechanism ceases to operate⁽¹⁵⁾. The electron density and energy (on which their speed depends) are functions of E/P ⁽¹²⁾ where E is the electrical field strength and P is the gas pressure. So for low pressure environment (where the discharge is self-sustaining) in order to increase the electron density and electron energy, the field strength (E) should be increased. The field strength, however, is given by $E = \frac{V}{d}$ ⁽¹⁸⁾ where V is the applied voltage and d is the gap between the electrodes. The field strength is of vital importance in practice because phenomena taking place on the cathode surface (Chapter 2.4.1) are closely related with its values.

2.4 Formation of Plasma State and its Properties

The discharges originate with the applied voltage accelerating the few electrons that are always present in a gas because of gas ionization by cosmic or other background radiation⁽¹⁸⁾. These electrons acquire kinetic energy as they are attracted to, and move towards, the positive electrode. Their passage through the electrode gap is interrupted by collisions with molecules after which they are re-accelerated towards the anode. Most collisions are elastic, with little change in energy between the particles in the encounter. Occasionally, by chance, a path opens for the accelerating electron which is long enough to enable it to gain sufficient energy to ionize the gas molecules on collision. The secondary emitted electrons resulting from these inelastic collisions are capable of further gas molecule collisions and thus the discharge can be multiplied⁽¹⁸⁾. The positive ions formed by the inelastic collisions drift back under the influence of the applied electric field towards the cathode and their subsequent neutralisation plays an important role in maintaining the electron emission and further gas molecule ionization. When the relatively heavy positive particles strike the cathode, electrons are ejected with considerable initial energy. It is these primary energetic electrons which play the predominant role in subsequent ionization.

Furthermore, the inelastic electron-gas molecule collisions in the discharge can also result in molecular excitation and dissociation into free radicals. These particles are extremely reactive chemically, and consequently have short life times in the discharge zone. They are believed to be a primary cause of the high chemical reactivity of the discharge. The excited states formed in the discharge also contribute

to some degree of chemical reaction. It is accepted that the changes in electron energy levels during excitation, ionization or recombination in the gas give rise to photon emission which causes the luminous zone characteristic of most electrical discharges. This is always observed in arcs and glow discharges. The colour of the discharge depends on the gas involved⁽¹⁷⁾. Thus the discharge can be seen to be a neutral plasma which is usually characterised by intense luminosity and in which are found electrons, positive and negative ions as well as atoms⁽⁴⁷⁾. Superimposed upon these is a complex series of activated species, neutral radicals and negative ions, all of which are potentially capable of chemical reaction⁽¹⁸⁾.

Examining the reactions of species which are available in a plasma generated by a glow discharge, it must be made clear that only molecular or chemical synthesis can be involved because the temperatures used are low ($T < 10^5 \text{ K}$) in comparison with nuclear synthesis where much higher temperatures ($T > 10^7 \text{ K}$) are employed, as Venugopalan reports⁽⁴⁸⁾. In a plasma, reaction between plasma particles and the material constituting the containing walls of the reactor and the electrodes can take place, as happens in ion plating deposition. Since ions and electrons are common species and even neutral particles have great kinetic energy in plasmas, plasma chemistry is quite different from ordinary chemistry. Atoms in highly excited states may react to give compounds which are unlikely to be formed in conventional chemical reactions.

Classifying plasmas from the aspect of thermodynamic equilibrium, there are three categories :-

- a) plasmas in complete thermodynamic equilibrium,
- b) plasmas in local thermodynamic equilibrium and
- c) plasmas in non-local thermodynamic equilibrium.

Plasmas generated by electron and photon beams as in the case of glow discharge belong to category c. Sometimes the local thermodynamic equilibrium plasmas are referred to as thermal or hot plasmas, and the non-local thermodynamic equilibrium as non-thermal or cold plasmas.

In this latter type of plasma, electrons and ions temperatures may differ by several orders of magnitude, whereas this is not the case in categories a and b. The main object of using a plasma is to achieve a high temperature by direct electrical excitation of the gas and thus provide a high energy capable first of dissociating and second of ionizing the molecules present. In principle, for reactions taking place in plasmas two distinct processes occur :-

- a) destruction of existing bonds of the molecules present, leading to creation of simpler molecules or free radicals, and
- b) formation of new bonds, resulting in the synthesis of bigger molecules.

Chemical bonds simply represent electron distributions between positively charged nuclei making up the cores of the atomic population of the molecule, mutually adjusted to yield maximum binding. These electron distributions exhibit varying topologies for different molecules. Therefore, the nature of the agency supplying the energy needed to maintain the plasma determines to some degree the efficiency with which particular bonds are broken or, conversely, the ease with which certain bonds can be created. A complication is that in any given type of reactor in which plasma reactions occur, there are

usually many different species which are simultaneously inducing the formation as well as destruction of bonds. Hence the net yield will be determined by the outcome of this competition.

Chemical synthesis, which involves rearrangement of electron distributions to form new bonds (molecules), may frequently be achieved more efficiently in glow discharges at low pressures.

The particles present in a low-temperature plasma - electrons, ions and neutrals - do not necessarily have the same temperature. A characteristic trend is that such differences become pronounced with decreasing pressure.

Conversely, with high pressures the temperatures of the plasma particles tend to equilibrate. Working temperatures ordinarily vary from near room temperature to 10^{40} K for atoms and ions. For the electron component the temperatures range from those descriptive of atoms and ions to upwards of 10^{50} K and more. Therefore, equilibration will lead to a considerable lowering of the electron temperature. If electrons are the means by which a certain reaction occurs an increase in pressure can have a deleterious effect on the net reaction yield. The effect of increasing pressure will lead to a greater frequency of energy exchange between the electrons, ions and neutral species, and will tend to adjust the electron temperature closer to that of the heavy particles. Thus with increasing pressure there will be an associated decrease in electron energy. If the electron temperature is greatly reduced, only a few electrons will have the required energy of activation to carry out the formation of the required bonds, and the yield will thereby be diminished⁽⁴⁸⁾.

In addition to pressure, other factors influence the electron energy distribution (which is believed to be a Maxwell-Boltzmann type) but its exact form is not yet clearly defined⁽¹⁸⁾. The electron energy distribution is concentrated around a definite maximum value which depends on gas pressure, field strength and collisional cross section. The electron energy distribution can be broken down into three different energy classes depending on the origin of the electrons :-

- a) The high energy primary electrons emitted from the electrodes as the result of positive ion component.
- b) The secondary electrons of lower energy emitted by the gas molecules as they are ionized by primary collisions.
- c) The much lower energy electrons, than those of the two first classes, which originate from other secondary processes.

The high energy electrons are those which are playing the basic role to activation and ionization phenomena which are taking place in the plasma. The ionization occurs when an electron, colliding inelastically with a neutral species, drives out an electron, suffering at the same time a reduction of its own energy equal to the amount given to the ejected electron. The non-radiative reverse process, which predominantly accounts for electron-ion recombination, is that in which two electrons collide in the neighbourhood of an ion. The electron with the reduced energy is simultaneously captured into the bound state of the neutral molecule. The latter is a three-body process, whereas ionization is a two-body process. The rates of both processes are proportional to the product of the number densities of the particles taking part in each. As a result at high pressures the recombination process is more favourable than the ionization process, so the number

of electrons tends to reduce at the higher pressures. Due to the reactive nature of plasma species, different reactions and interactions occur in the bulk plasma, on the walls and the electrodes of the reactor. Since the intention of the present work is to coat the cathode-specimen it is reasonable to examine the phenomena which are taking place on the negative electrode.

2.4.1 Cathode Interactions due to Plasma Presence

When the negative electrode is subjected to a high energy ion bombardment a number of different effects can occur. The most important are.

Alloying of the Cathode Element. When positively charged ions moving down the electric-field gradient collide with the cathode surface atoms, combinations of dissimilar atoms may take place. For example, a bombarding ion with adequate energy and small enough cross-section can penetrate the lattice of atoms forming the cathode solid surface and lodge internally, forming an alloy. Barriers of the order of 10ev must be surmounted to push atoms from a favoured position to another metastable position in the lattice (interstitial position). Energies of this level are available in discharges like a glow, spark or high energy arc to effect the alloying of the cathode element and the bombarding ones. This phenomenon is sometimes referred to as ion implantation.

Sputtering of the Cathode Surface. Instead of simple penetration the impacting ion after penetration may drive one of the native cathode ions from its preferred position to an interstitial position. If there is sufficient energy, the penetrating ion may produce additional displaced atoms before coming to rest. A following ion may then succeed in

dislodging some of the dislocated native atoms which can subsequently move out of the parent lattice or knock out one of the surface atoms. The new lattice alloy, formed by the sputtering process is one in which there are dislocated native ions and normal vacancies (Frenkel defects). Foreign bombardment ions can terminate also by occupying vacant lattice positions.

Broadening of the Oxidation Zone. If the cathode originally has an oxide layer on the surface, the bombardment of ions may cause a reduction of the oxygen in some of the oxide groups with the subsequent oxidation of some of the deeper lying lattice ions.

Annealing. If the cathode lattice already possesses dislocations and it is subjected to ionic bombardment with energies insufficient to cause penetration then this may result in disappearance of dislocations by the mechanism of vibrational shaking of the lattice through collisions which are taking place at the surface.

Etching. As in chemical etching, ionic bombardment can remove surface atoms from favourable sites. Such sites usually are the grain boundaries. It can be said that ionic bombardment can substitute or complement the chemical etching because it can provide sputter etched surfaces whose atoms become excited in collisions. Thus the sputter etched surfaces may well be more reactive than the normally prepared surface of the material.

Surface Reactions. The ions coming into the surface of the cathode may react with each other as a result of the collisions with the surface. The process resembles three-body ion-electron recombination. Incoming

ions can also give up their excess energy to the surface lattice, neutralize charge, and combine with each other (surface recombination). If this combination does not occur during deposition, subsequent ionic bombardment can provide the required activation energy, and thus the reaction can be completed.

CHAPTER 3
THE ION PLATING PROCESS

3.1 Introduction

The ion plating is one of the physical vapour deposition processes and is more recent than vacuum evaporation (metallizing) and sputtering. It was only in 1963 that the originator of the method, Mattox, reported the technique, and since then much work has been done and many relevant papers have been published. The stimulus for such a great interest was the advantages which this method shows in comparison with the other two methods.

Comparing the methods as shown in the table 3⁽⁶³⁾, the superiority of the ion plating can be seen to lie in the adhesion and uniformity of coatings. At the same time ion plating retains all advantages of the vacuum deposition processes, i.e.

- a) Lack of contamination due to the exposure of the part to be coated to reactive gases or liquids. For example, hydrogen embrittlement is not encountered⁽⁵⁾. Generally ion plating deposits are of very high purity.
- b) Complete control over temperature of the part to be coated, so that it can be kept at room temperature, or can be heated or cooled, as required. Thus temperature sensitive materials such as aged or hardened alloys, salts, rubbers and plastics can be coated.⁽⁵⁾

Characteristic	Coating Technique				
	Electroplating	Vacuum Evaporation	Chemical Vapour Deposition	Sputtering	Ion plating
Materials capable of deposition	Elemental metals	Elemental metals some compounds	Elemental metals some compounds	Metals, alloys, compounds, cements, ceramics, polymers.	Metals, alloys, some compounds
Nature of processes	Electrochemical	Vacuum evaporation	Chemical Reaction in vacuum.	Vacuum plasma	Vacuum plasma
Nature of film	May contain pores can blister	May not be uniform	Dense, pore free	Dense, Fairly pore free.	Dense, pore free does not blister
Adhesion of film to surface	Fair	Poor	Good	Good	Excellent
Type of interface	Sharp between coating and substrate (possible hydrogen embrittled substrate)	Sharp between coating and substrate unless thermally diffused.	Diffused	Relatively sharp	Diffused or Graded
Uniformity of film	Fairly uniform on flats, can have non uniformity on edges	May very	Good uniformity	Fairly good uniformity	Good uniformity
Film purity	May contain bath salts and gaseous inclusions	Purity of starting material	Purity of starting material	Purity of starting material	Purity of starting material
Deposition rates	moderate	Very fast	Relatively slow	Relatively slow	Very fast
Film thickness control	Fair	Poor	Good	Excellent	Excellent
Size of object that can be coated	Limited by size of bath and power supply	Limited by size of vacuum chamber	Limited by size of vacuum chamber	Limited by size of vacuum chamber	Limited by size of vacuum chamber.
Complex geometric surfaces	Can be coated but not uniformly	Only surfaces facing source are coated	Coverage of all surfaces	Coverage of all surfaces	Complete coverage of surfaces
Equipment required	Chemical baths, controls and power supply	Vacuum chamber and heat source	Vacuum chamber and heat source	Vacuum chamber & dc or rf power supply	Vacuum chamber, heat source & high voltage supply
Ecology problem	Chemical handling vapours & disposal	None	None	None	None

TABLE 3. Generalized comparison of various coating deposition techniques.

In considering the use of physical vapour deposition methods in metallurgically oriented technology, a prime economic consideration is the deposition rate. Bunshah⁽⁵⁰⁾ reports that the deposition rates for the three processes, with present day technology, are as follows :-

<u>Process</u>	<u>Deposition rate per minute</u>
Vacuum Evaporation (Metallizing)	2,5 to 75 μm (in special cases 200 μm)
Ion Plating	2,5 to 25 μm
Sputtering	10^{-2} to 10^{-1} μm (in special cases 1 μm)

From the above table it can be seen that ion plating has a deposition rate not quite as good as that of vacuum evaporation but better than that of sputtering.

Another important advantage of ion plating is the grain structure of the films obtained⁽⁵¹⁾. The grain size of ion plated coatings is very fine (1 μm or less) so strength and touchness of the coating is increased compared to other methods such as solid solution or precipitation, where strength is increased at the expense of toughness⁽⁵⁰⁾. Finally, the surface finish is equal to or better than that of the substrate.

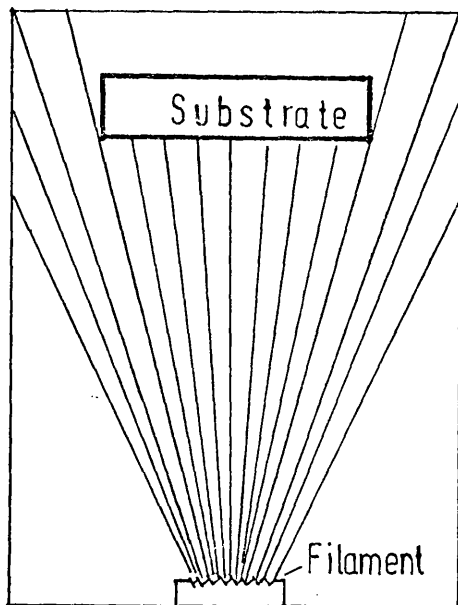
The above given advantages make the ion plating process a very attractive one but there are certain disadvantages of the method that should also be mentioned.

- a) Difficulty of masking to block coating of certain areas of some parts because of the great "throwing power" of the method.
- b) Lack of direct deposit-thickness monitoring instruments during the deposition.
- c) Limitation on the maximum size of the specimen which can be coated by ion plating. This is determined by the physical

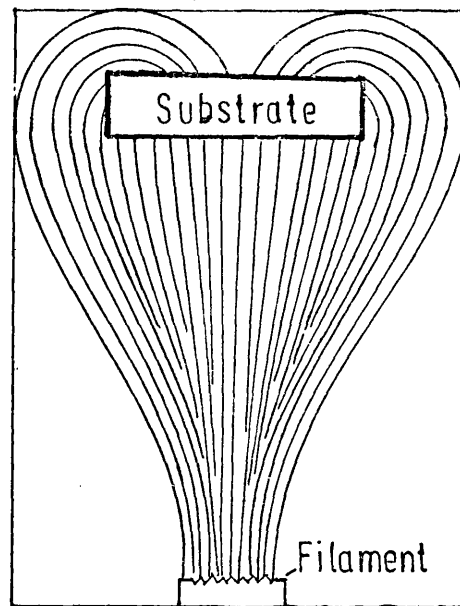
size of coating chamber and the availability of high voltage supplies capable of sufficient power. However, ion platers with 200kW electron beam guns with energy supplies of over 40kW capable of coating surfaces 50cm by 50cm approximately are now available⁽⁵¹⁾.

As already mentioned, the main advantage of this method is in the properties of the resulting coating, and in particular its adhesion and uniformity which is the result of good "throwing power" of the method. "Throwing power" is the ability to coat simultaneously and uniformly all exposed surfaces without part rotation^{(9),(52)}.

In ion plating, the object to be plated is the termination point for an electric field which exists between the evaporation source and the object. There is a potential difference between any point on the object and the source. Once the evaporant is ionized in the discharge, the charged ions follow the electric lines of force (Fig. 3b) to all points on the specimen surface, if shielding effects are not present, whereas normal evaporation, for instance, will only give line-of-sight coverage (Fig. 3a). As a result, it is possible to obtain uniform film over the entire surface of complex configurations (threaded bolts, springs, rings, notched specimens, internal surface of tubes etc.)^{(22),(53)}. Thus it can be seen that ion plating is not just a direct line-of-sight coating process⁽⁵²⁾. The uniform distribution of the film over the entire surface of the material is apparently due to the fact that the cathode dark space, which acts as the effective source of the evaporant, completely surrounds the object to be plated⁽⁵⁴⁾.



a) Partially plated substrate by conventional vacuum deposition.



b) Completely plated substrate by Ion plating.

FIG.3. Comparison of conventional vacuum-deposition with ion plating techniques.

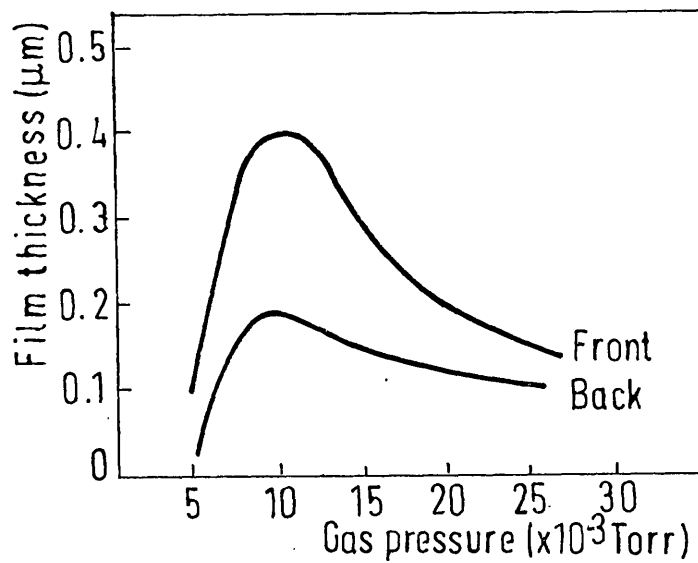


FIG.4. Film thickness of front and back surfaces of a flat plate specimen as a function of argon pressure (after D.G. Teer).

However, more recent investigations have proved that the good "throwing power" should not be attributed to electrical force lines alone. From information provided by literature it can be seen that the degree of ionization in many plasmas is very low, (0.1% to 2.0%) (16),(55),(56). With such low degrees of ionization, most of the deposited material is likely to be due to arrival at the substrate of energetic neutral atoms, rather than ions. Chambers and Carmichael⁽⁵⁾ give details of relative thickness of films deposited onto the front, back and inside surface of different configuration samples as a function of pressure, with the rest of the ion plating variables constant. It was found that the ratio of film thickness on the front surface to that of the back and that of inside surfaces approaches unity only at gas pressures higher than 30×10^{-3} Torr. Below this pressure limit this ratio is far below unity. Confirmation of these results was provided by Teer and Sherbiny⁽⁵¹⁾ whose results are shown in Fig. 4.

According to the latter the field has only a minor effect and the "throwing power" is due to the gas scattering effect. Bunshah⁽⁵⁰⁾ supports this argument. Finally, Aisenberg and Chabot⁽⁵⁷⁾ consider that probably the bigger contribution to the high "throwing power" of ion plating is due to the gas scattering effect. This raises the question of the effects of ambient gas pressure during deposition. Ion plating occurs typically at pressures above 10^{-3} Torr, which are much higher than those used in vacuum evaporation. Thus the deposition material encounters multiple collisions with the background gas on its way to the substrate. Deposition material is thus scattered around the substrate so that all surfaces are coated.

From the standpoint of adhesion, as Mattox⁽⁹⁾ states, the principal benefits obtained from the ion plating process are the ability to

- a) sputter clean the surface and maintain it clean until the film begins to form,
- b) provide a high energy flux to the substrate surface, giving a high surface temperature thus enhancing diffusion and chemical reactions without necessitating bulk heating, and
- c) alter the surface and interfacial structure by introducing high defect concentrations, physically mixing the film and substrate material, and influencing the nucleation and growth of the depositing film.

Adhesion is a macroscopic property which depends on three factors:

- a) bonding across the interfacial region,
- b) type of interfacial region (including amount and distribution of intrinsic stresses) and
- c) the fracture mechanism which results in failure.

Summarising the above it can be said that during the ion plating process the substrate surface is cleaned continuously by the action of sputter cleaning, providing an atomically clean metal surface with a high concentration of defects. This effect, with the assistance of the high energy atoms which strike on the surface, improves the bonding, forming a chemical graded junction between substrate and coatings. The creation of such graded layer is the result of mixing in the interface region of different "plasma" species which according to Mukherjee et al⁽²⁹⁾, can occur by:

- (i) penetration of energetic ion and neutral atoms (accelerated by collisions with energetic ions) of the coating material

into the substrate lattice, and

- (ii) the co-deposition of substrate atoms which were sputtered and reflected back to the substrate either by scattering or by ionization in the plasma and bias-field acceleration.

It should be added that the heating of the substrate, which occurs as the result of the ion bombardment, also aids mixing by increasing the surface and bulk mobilities of deposited atoms.

The energies acquired by the ions as they are accelerated through the discharge were believed to be between 3 and 5 keV⁽⁵³⁾,⁽⁵⁸⁾ and they depended strictly on the potential directly applied across the electrodes. However, Davis and Vauderslise⁽⁵⁹⁾ have demonstrated that the ions striking the cathode of a glow discharge have a wide range of energies up to that corresponding to the full cathode fall of potential. The determining factor for each ion species appears to be the ratio between the mean free path for collision and the cathode dark-space distance. When the mean free path is relatively large, many of the ions manage to traverse the cathode dark-space with few or no collisions, and thus the high energies predominate. When the mean free path is small most of the ions have their last collision close to the cathode and so they cannot regain much energy before hitting the cathode. Their acceleration is small due to the fact that they travel through only part of the cathode fall, resulting in predominantly low energies ions.

On the basis of the above argument, Teer⁽⁵¹⁾ proposes that the mean energy of the striking ions is about 300 eV which is much smaller

than that originally suggested, but still high enough to penetrate into the lattice, since, according to Wehner and Anderson⁽⁶⁰⁾ ions become embedded in the lattice at kinetic energies greater than 100eV. The same is argued by Kaminsky⁽⁶¹⁾ who cites that bombardment of a nickel target by helium, with ion energies of about 100eV, causes incorporation of helium ions into the interstitial spaces of nickel lattice. This high energy bombardment also causes enhanced diffusion since it provides the activation energy needed for diffusion at the surface even without heating the bulk substrate. The ion bombardment may further enhance the diffusion by increasing the defect concentration⁽⁶²⁾ at the surface region and by producing a high density of vacancies in the sub-surface regions⁽⁵¹⁾.

In addition to these factors influencing good adhesion it should be noticed that heating of the substrate due to ion bombardment and other sources of heat occurs⁽⁵²⁾. According to Krutenat⁽¹²⁾ the energy input to the substrate, as a consequence of the electrical bias and resulting discharge, is utilised mainly in heating the substrate. Approximately 95% of the kinetic energy of the ion bombardment is converted into heat. Thus, according to the experimental details used he measured temperatures of up to 750-950⁰C.

Another advantage of the ion plating technique is that coatings obtained often have a density approaching that of the bulk density of the coating material. There are several reasons for this:-

- a) due to sputter cleaning before and during deposition, any loosely-fitting atom in the film lattice is sputtered away

because the bond force keeping it in the lattice is small, so it is easily dislodged by the action of high energy bombarding species.

- b) the negatively charged substrate attracts a considerable flow of positive ions and energetic neutrals which impart their high energy to the surface. The transferred energy and momentum⁽⁵⁷⁾ helps surface atoms to flow and nucleate into better crystallographic sites, thus giving better adhesions and non-porous films.
- c) collisions between deposition atoms and gas atoms can result in agglomeration of the deposition materials. In the case of other vapour deposition methods (e.g. vacuum evaporation) these agglomerates arrive at the substrate and give rise to granular films with a number of voids between them, as a result of their arrangement.

However in the case of ion plating, these agglomerates become negatively charged and hence repelled from the negatively charged substrate, so that deposition of incoherent granular coatings is avoided⁽⁵⁶⁾. The agglomerates become negatively charged by the same mechanism which causes negative charge to insulating surface when introduced into the plasma region. This is because the electron and ion densities of the plasma are very nearly the same, while the electron mass is much smaller than that of the ion mass and thus their respective mobilities are different. As a result, the random electron particle current density is orders of magnitude greater than the

random positive ion particle current density, so an insulating surface introduced into a plasma will receive a much larger random current electron density than random ion current density. The insulating surface will therefore charge up negatively to a potential where enough of the incident electrons are repelled so that net ion and electron currents are zero⁽⁵⁷⁾.

Finally, the advantage of the high purity obtained should be emphasised. As already mentioned, the ion plating films are of high purity because they are not exposed to reactive gases or liquids, as happens with electroplated films. This high purity is a general characteristic of all vacuum vapour deposition methods. The governing factor for a high purity coating remains on the purity of the source material(s). If the source materials are carrying or include impurities it is inevitable these impurities to be introduced into the film. Since ion plating operates with a continuous flow of inert gas and since it is preceded by a period of sputter cleaning then the influence of residual gases evolved from the chamber walls is minimized. Thus the only source of contaminants is material of used filaments, or boats, which support the evaporant, as in conventional ion plating of low melting point materials. However, even this contamination can be eliminated if an electron beam source is used, as in the cases of reactive ion plating of refractory materials. Furthermore, in the case of chemical ion plating, (as in the present work), the problem of contamination is a minor one since the method does not use any

filament or boat, and the coating materials are gases. So their purity ensures the purity of coatings.

3.2 Technical data on a typical Ion Plating process

A typical ion plating arrangement is illustrated in Figure 5. Firstly the system is evacuated to 10^{-6} Torr to reduce the contaminating gases to the lowest possible levels. The substrate is made the cathode of a diode-type d.c. gas discharge, and the high voltage lead to the substrate is carefully shielded to prevent metal deposition on the insulator during the plating operation. The anode of the discharge circuit is attached to the metal deposition source - typically a resistively heated refractory boat or filament of tungsten. A high voltage d.c. power supply with a high reactance such as is normally used for sputtering, is used in ion plating. The high reactance of the power supply limits the current in the cathode circuit and thus assures discharge stability. The discharge gas is admitted in through a needle valve, and the pressure in the system is monitored by means of suitable gauges.

In a typical operation the substrate is precleaned and placed in the vacuum system. The system is then evacuated to pressures 10^{-6} Torr and the evaporant premelted. The system is then backfilled, usually with argon to a pressure between 1×10^{-3} and 50×10^{-3} Torr, while the d.c. gas discharge is established at between 2 and 5 kV with a cathode-substrate current density of approximately 0.5 mAcm^{-2} . The substrate is then sputter cleaned for a period of time depending on the material and surface conditions (usually between 20 and 30 min.). After this cleaning stage the evaporator boat or filament temperature, is slowly raised until the material begins to evaporate, and then the material starts to deposit on the substrate. The important step is to form the surface coating interface during the ion bombardment in order to give good adhesion. The rate of evaporation should be much higher than that of the sputtering which takes place simultaneously as the deposition proceeds, in order to

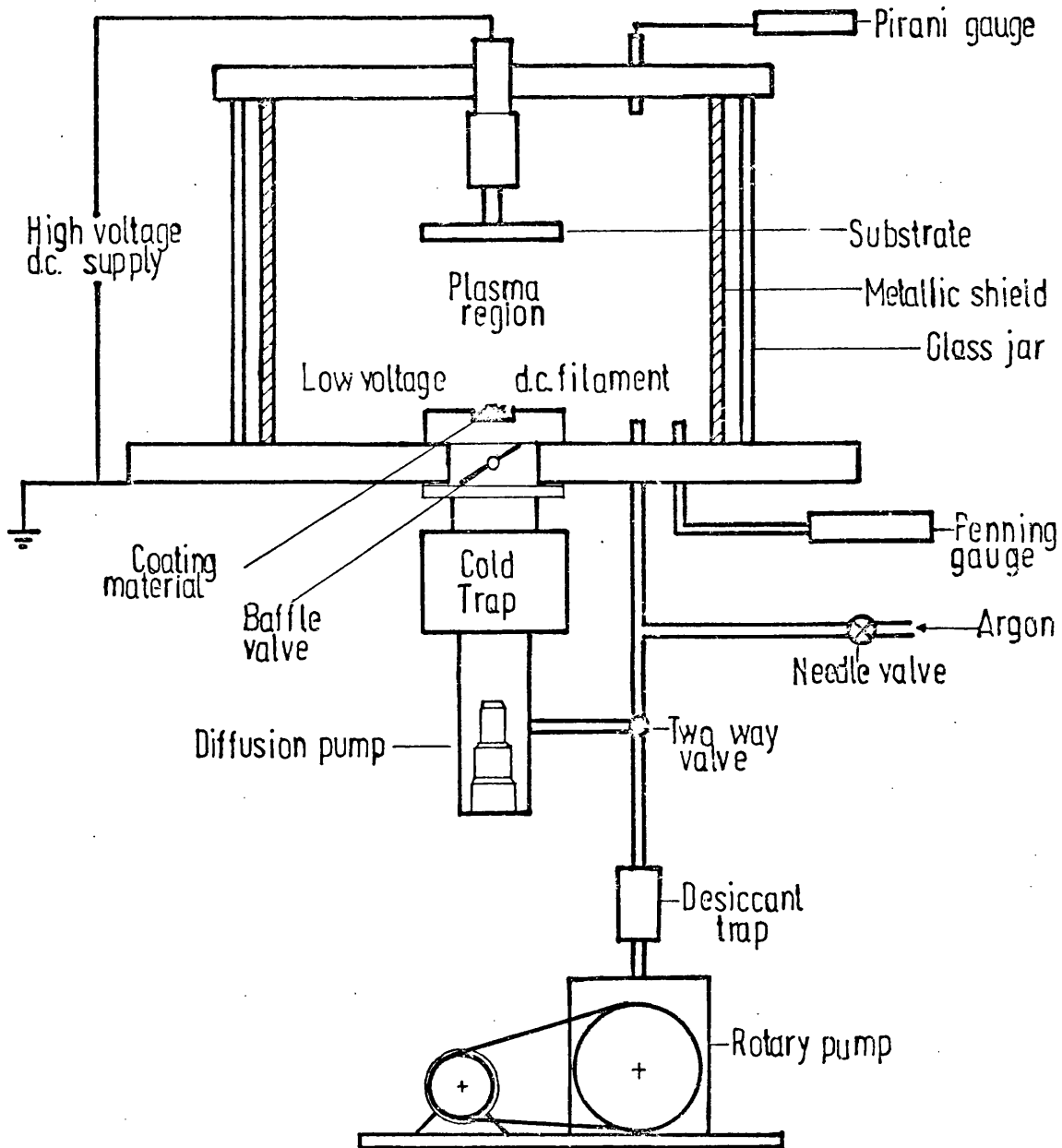


FIG. 5. A typical Ion plating apparatus..

form a coating. In conventional ion plating it is possible after the formation of the interfacial region, the system to be evacuated again and the film thickness to be increased by vacuum evaporation.

As already noted an important role during the ion plating is played by the source providing the material for the coating. If this material has a low melting point such source could be a resistive heating one. If on the other hand, refractory material with very high melting point is the candidate for coating material more sophisticated sources are needed such as electron beam gun, plasma evaporation torch⁽⁹⁾ or even arc arrangement⁽⁵⁶⁾.

In cases where a precious material is to be the coating e.g. gold or silver where it is desirable to avoid losses of the precious metal another ion plating technique is used assisted by sputtering. The sputtering target-anode is the metal and the substrate is the cathode, so that a higher fraction of ionization is obtained than in the case of resistive heating⁽⁶⁴⁾. Due to the higher degree of ionization the ionized material following the electric lines are deposited only on the termination points at the cathode, without any losses on other parts of the apparatus.

In another type of ion plating, the reactive ion plating process, it is possible to deposit compounds instead of simple metals on the substrate. In this process evaporated metal reacts with constituents of the ionized atmosphere gas, and the argon of the conventional ion-plating is replaced completely or in part by reactive gas. Reactive gases which can be used for reactive ion plating can be, oxygen for oxides, nitrogen or ammonia for nitrides, hydrocarbons for carbides. By controlling the deposition parameters

it is possible to control the stoichiometry of the reaction.

Finally, an alternative technique to the evaporation has been developed in which a metal-bearing gas and reactive gases like hydrocarbons, nitrogen or ammonia, e.t.c. are introduced into the glow discharge and different chemical reactions can be made to occur by altering the parameter used. This technique has been termed "chemical ion plating".

The techniques described above can only be used with conducting substrates. However, when insulators are to be coated the glow discharge has to be maintained indirectly around the workpiece by using a Faraday cage. In this arrangement the substrate is positioned in an open mesh wire cage, which is connected to the high voltage lead and the resultant glow discharge produced by the cage provides the positive ions required for the bombardment of the substrate. During deposition the evaporated metal readily passes through the mesh to the substrate. Contamination of the substrate by sputtered cage material can be avoided by making the cage from the coating material or ion plating the cage with the coating material prior to its use.

An alternative approach to coating non-metallic substrates is to use an R.F. bias⁽⁶⁵⁾ instead of the D.C. bias. Two advantages are gained in this way. Firstly, an R.F. bias enables the plasma to be maintained at a much lower pressure, down to 10^{-4} Torr⁽⁶⁵⁾. Secondly, this bias causes a change in the discharge anodic parts which prevents the charge build-up on the non-conducting surface. This results in constant sputter cleaning before and during the film deposition. By this method it is possible also to deposit non-conducting layers without glow discharge extinction occurring.

The R.F. discharge also can be used in the same way as the D.C. process for production of compounds by chemical reaction of metal bearing gases with oxygen, nitrogen or ammonia. In this way silicon oxide is produced by the use of silane and nitrous oxide⁽⁶⁶⁾ or silane and oxygen⁽⁶⁷⁾, silicon nitride from silane and ammonia⁽⁶⁸⁾.

3.3 Operating Parameters in Ion Plating

In the ion plating process, there are various parameters which influence coating characteristics. These are :-

- a) Gaseous discharge pressure
- b) Substrate voltage
- c) Current
- d) Feeding rate of coating material(s)
- e) Ratio of amount of reactants used
- f) Substrate temperature
- g) Distance of electrodes
- h) Substrate geometry

The glow discharge pressure and the feeding rate of coating material(s) are the principal parameters in the ion plating process. They affect both the ion deposition efficiency and the uniformity of the coating. Chamber and Carmichael⁽⁵⁾, using copper substrates and gold as evaporant materials to investigate how variations in processing parameters affect uniformity of coatings, conclude that uniformity increases as discharge pressure increases and decreases as coating rate increases.

Wan et al⁽⁵²⁾, investigating the influence of different ion plating processing variables, used stainless steel as substrates, copper as coating material and carried out their experiments in argon gas glow discharge. This combination was used because, under the experimental conditions, these materials do not interact unless temperatures are excessive. The substrate temperatures were intentionally held low in most of that work, because if the substrate temperature approaches 300° to 400°C, the temperature effects were more significant

to the microstructure than any of the other process conditions.

Furthermore, in order to characterize the deposited coatings according to their microstructural morphology they defined a relative scale of Figure of Merit, as shown in Fig. 6. This classification is based on the grain shape, orientation, and size, the surface topography and the density of the deposit. A coating which had the microstructural characteristics of a smooth surface, small and equiaxed grains, and high density was rated 100 on the scale. A coating which had a rough surface topography, large columnar grains, a relatively large amount of microporosity was rated zero on this scale. This scale was used in evaluating the deposits to describe the effects that the variation of deposition parameters had upon the coating morphology. Coatings with a Figure of Merit of 100 could be produced with diode bias techniques using suitable parameters. Their experiments showed consistent relationships between the deposition variables.

Figure 7 shows the relationship between the deposition rate and the Figure of Merit. From this it can be seen that, as the deposition rate is increased, the Figure of Merit decreases. If the deposition rate is held constant, the Figure of Merit decreases as the pressure increases, and it increases as the substrate power density increases. Temperature and high substrate bias voltage affect these relationships.

Figure 8 shows the relationship between the argon pressure and the morphology of the deposit as expressed by the Figure of Merit. It can also be seen that, as the pressure is increased, the Figure of Merit decreases. If the pressure is held constant, the Figure of Merit decreases as the deposition rate increases, and it increases as the

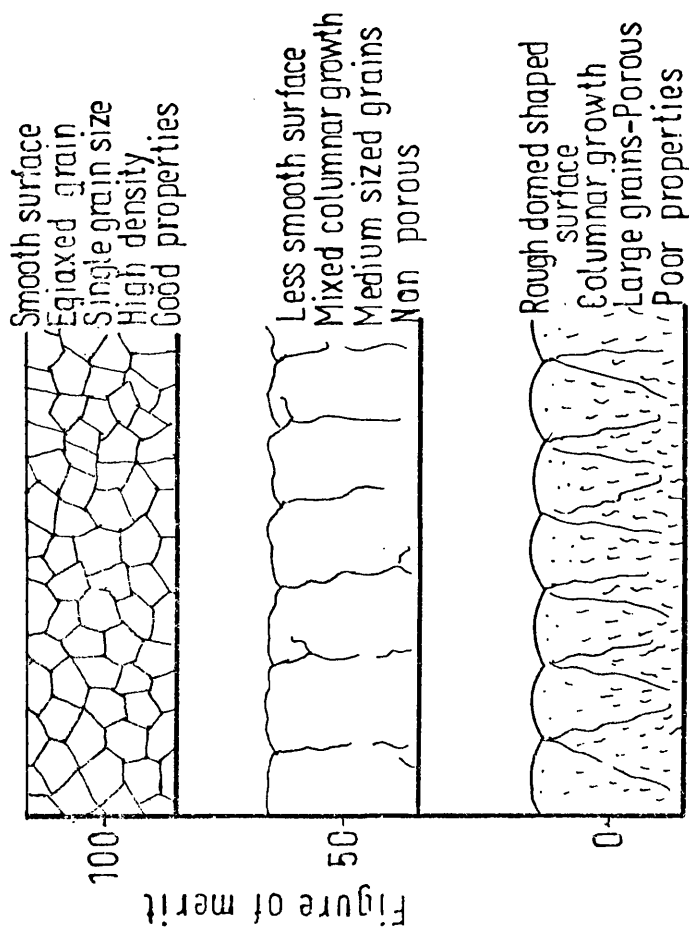


FIG. 6. Figure of Merit describing the morphology of deposited coatings.

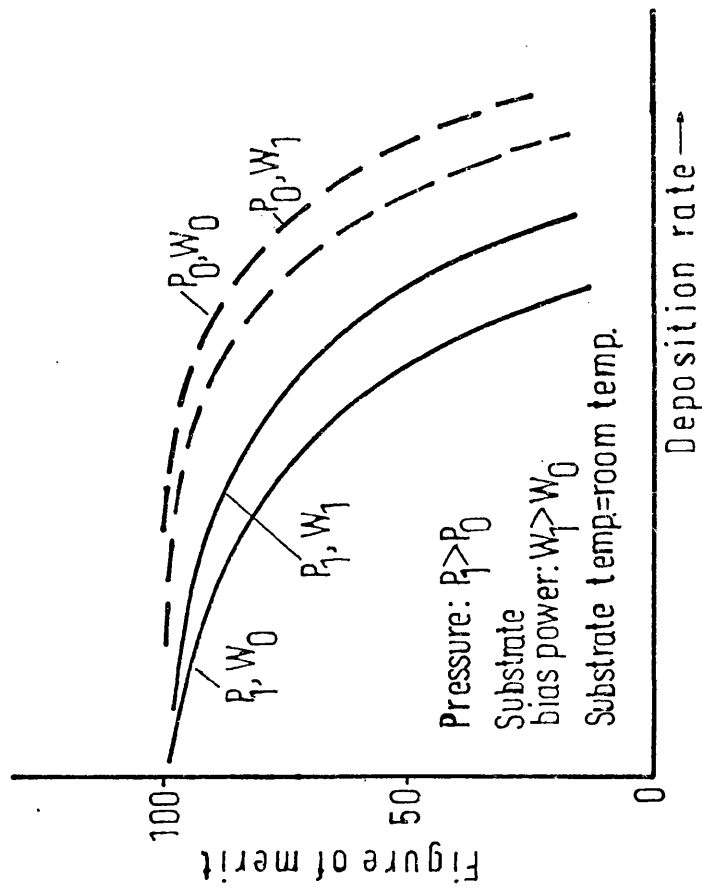


FIG. 7. Relationship between the deposition rate and the Figure of Merit describing the morphology of deposited coatings.

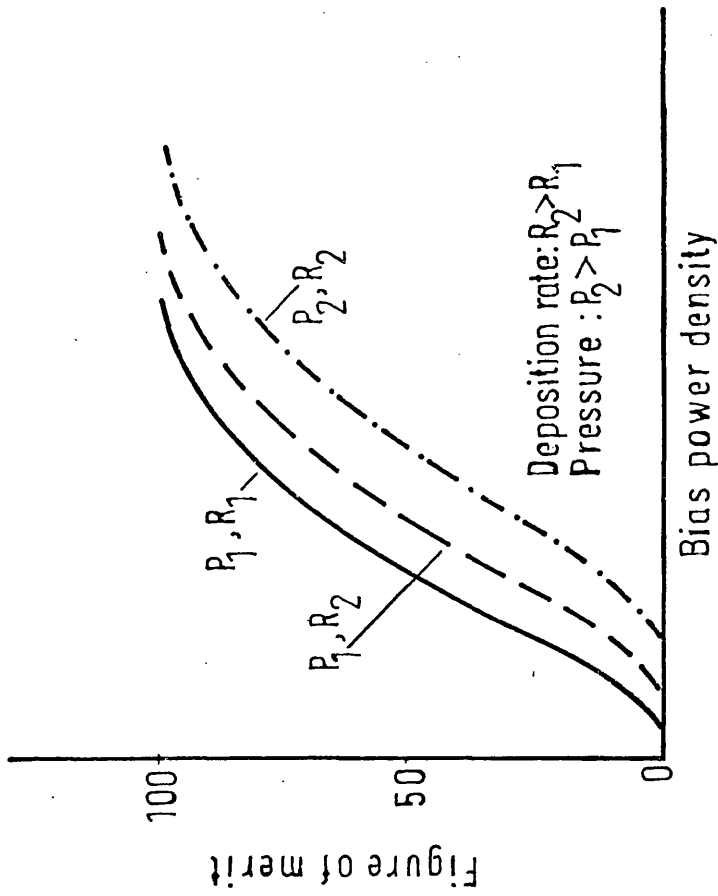


FIG. 9. Relationship between the bias power density and the Figure of Merit describing the morphology of deposited coatings.

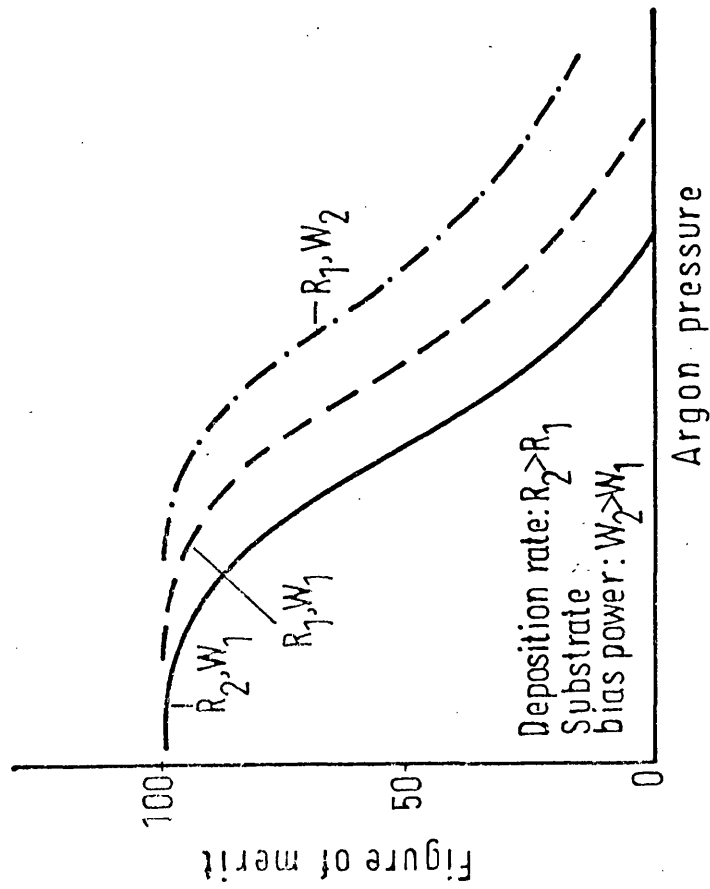


FIG. 8. Relationship between argon pressure and the Figure of Merit describing the morphology of deposited coatings.

substrate bias power increases.

Figure 9 shows the relationship of the substrate bias power density and the Figure of Merit. Finally it can be seen that as the bias power density is increased the Figure of Merit increases. If the bias power density is held constant and the pressure and the deposition rate are increased, the Figure of Merit decreases.

CHAPTER 4

EXPERIMENTAL APPARATUS-MATERIALS

The experimental apparatus was originally an electron beam zone refiner which had been modified for the purpose of "chemical ion plating". This is illustrated in Fig. 10 and Fig. 11. Basically this consisted of three main parts :-

1. The coating chamber
2. The vacuum system
3. The electrical circuits and high tension supply

The basic requirements of the vacuum apparatus used for routine coatings production generally are :-

- a) High pumping speeds
- b) Minimum back streaming
- c) Demountable system for ease of maintenance

4.1 The Coating Chamber

The reaction chamber was a watercooled cylindrical stainless steel vessel of internal dimensions 47cm in height and 21cm in diameter. Watercooling is probably advantageous because it does not allow desorption of gases from the walls as may happen with other materials such as glass⁽¹⁵⁾. This chamber was located on a pedestal of the same stainless steel and was vacuum-sealed by the assistance of an 'O' ring. On this pedestal were also located a number of vacuum-sealed current leads. One of these was replaced by a needle-valve-controlled reactant inlet which was extended to the top of the chamber. A second needle valve was placed on the top of the vacuum

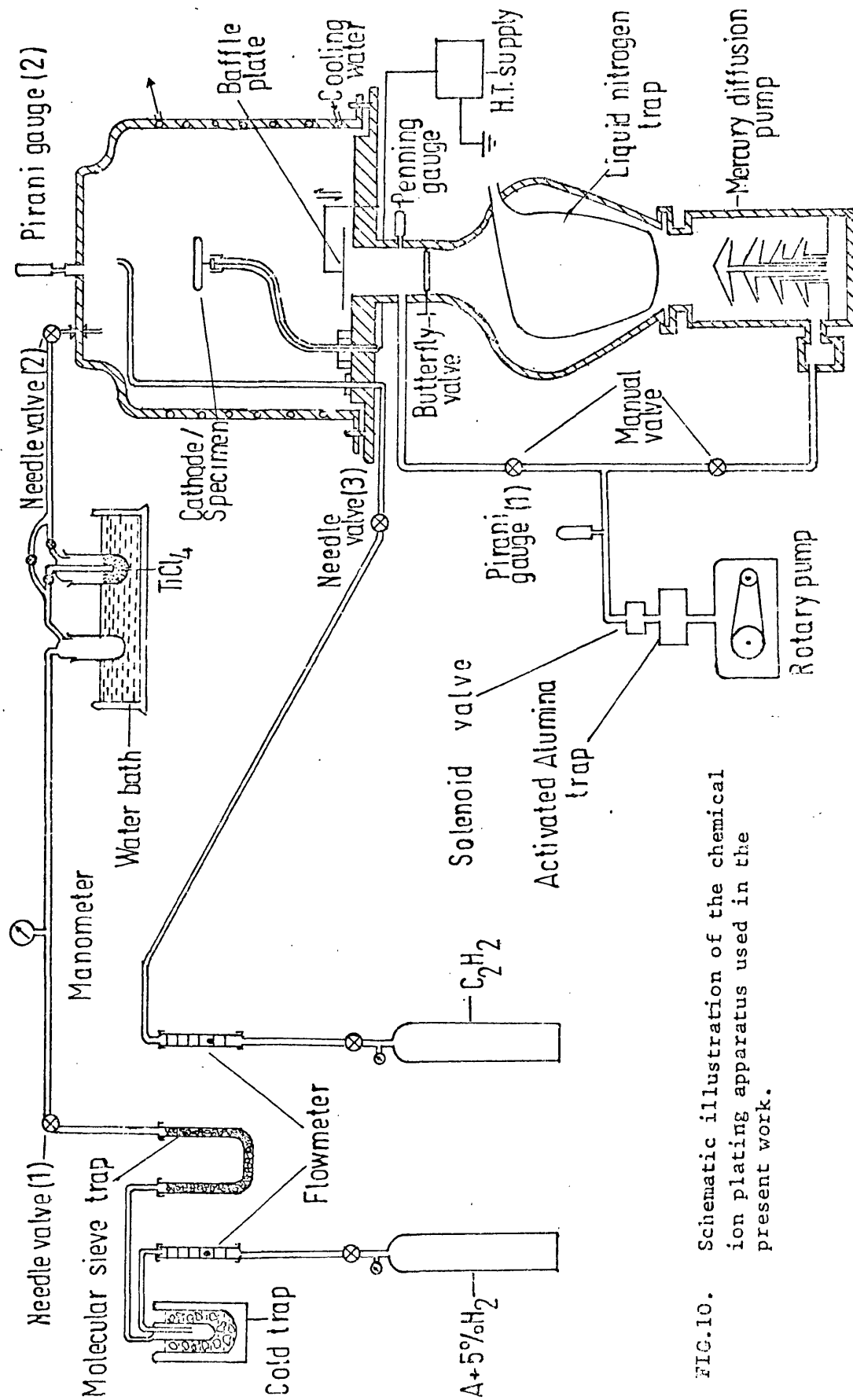


FIG.10. Schematic illustration of the chemical ion plating apparatus used in the present work.

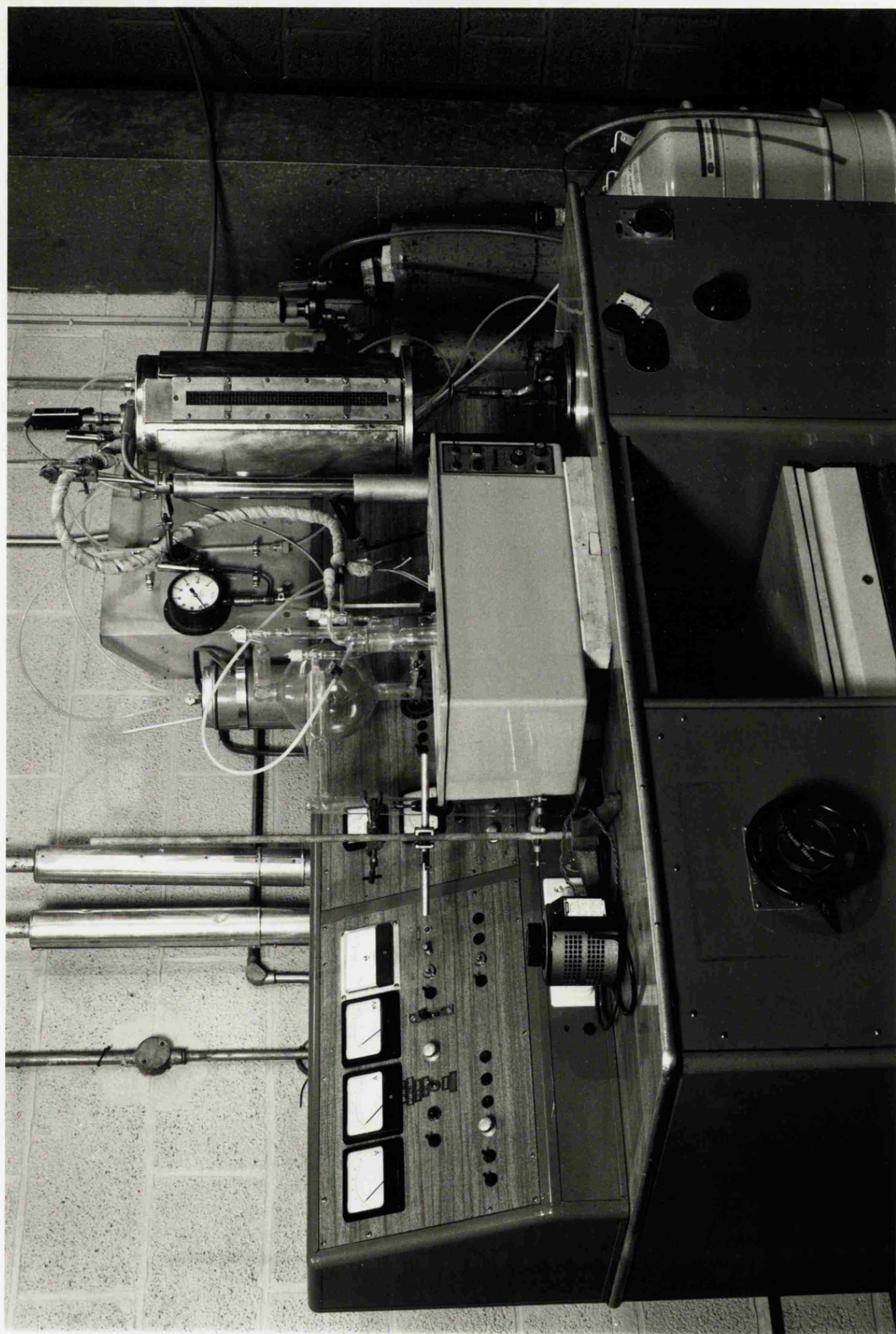


FIG.11. Photograph of the chemical ion plating apparatus used in the present work.

chamber. Both the gas inlets had their orifices near the top of the chamber, away from the pump aperture, thus aiding mixing of gases before they flow through the plasma region. Chamber pressure was monitored by a Pirani gauge fitted at the top of the bell jar. Gas flows were measured with "Meterate" flowmeters.

Using the pumping system the residual gas was pumped down to a pressure of 5×10^{-4} Torr. Subsequently, utilizing the flowmeters and needle valves, the system was backfilled with reagents to 10^{-3} - 6×10^{-2} Torr. This pressure was maintained constant during the whole plating procedure by balancing the pumping speed and the inlet rate. The stability of pressure was of vital importance because otherwise the current of the discharge varied and thus the deposition characteristics were disturbed, leading to non-uniform coatings.

When selecting the different materials for tubing, flowmeters, needle valves etc., problems arose because of the highly reactive nature of titanium tetrachloride. For example, flowmeters made of "Kematal" (Acetal plastic supplied by G.A. Platon Ltd.) were destroyed immediately when they came in contact with titanium tetrachloride. Silicone gaskets (provided by "Sovirel") used in washbottle and other connections were similarly destroyed. It was found that P.T.F.E.-covered silicone gaskets ("Quick-fit" provided by Gallenkamps) were adequate. Also viton was initially inert but degraded after prolonged contact with titanium tetrachloride. Materials which were resistant to titanium tetrachloride were glass, nylon, P.T.F.E., brass, copper and stainless steel.

A further problem in the initial stages was the blocking of the needle valve admitting the titanium tetrachloride. During blocking the pressure in the chamber gradually decreased, with a consequent decrease of the discharge current. Such an effect could appear within a few minutes of starting admission of the reactant into the chamber. Blocking was the result of accumulation of a yellow solid material. This problem was overcome by using an improved design of gas bubbler (described in Chapter 4.1.1) and by using a P.T.F.E. needle and seat, which prevented adhesion of solid material on these parts.

The reaction chamber was originally connected to the pumping unit by means of a butterfly valve but this was unsatisfactory under the present conditions for two reasons.

- a) It was difficult to stabilize the pumping speed of the vacuum system. This led to pressure fluctuations and hence instability of the discharge current.
- b) It was difficult to obtain the same pressure readings day to day because exact valve settings were difficult to reproduce.

The system was modified by incorporating an adjustable baffle plate above the butterfly valve, so that pumping speed could be throttled accurately and both chamber pressure and discharge current became adequately controllable.

4.1.1 Admission of Titanium Tetrachloride to the Vacuum Chamber

Due to the reactive nature of titanium tetrachloride, precautions were necessary to maintain a stable flow to the chamber (as already noted). Removal of water from the carrier gas and suppression of leaks was important, otherwise solid deposits formed in the sintered glass bubbler and also in the needle valve. This was accomplished by

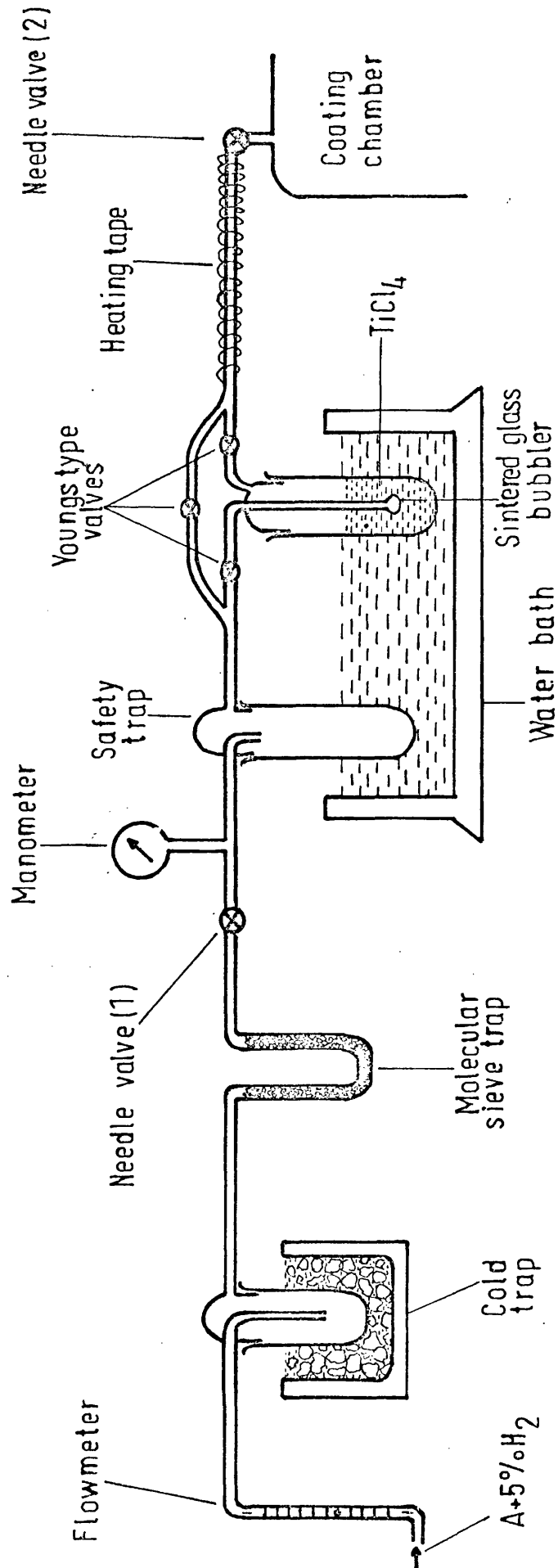


FIG. 12. Schematic diagram of the admission line of titanium tetrachloride to the vacuum chamber.

the use of a molecular sieve trap preceded by a cold trap at -78°C , as can be seen on Fig. 12.

To ensure stable gas flow it was necessary to adopt two stages of pressure reduction. Needle valve (1) (Fig. 12) served mainly to set the carrier gas flow rate. The section between needle valve (1) and (2) was maintained at a constant pressure of 350 Torr. Because pressure drop was small this second valve gave good control of the final chamber gas composition. Blocking of this needle valve could be easily detected by a change of the manometer reading. The line between the bubbler and the chamber was maintained at about 100°C to prevent condensation of titanium tetrachloride. Finally, a by-pass line and safety trap were used to prevent sucking back of the titanium tetrachloride. The bubbler assembly was maintained at 60°C in a thermostatically controlled water bath.

4.2 The Vacuum System

The vacuum unit consisted of a rotary pump having a pumping speed for air of 210 l min^{-1} , and a mercury diffusion pump of a pumping speed of 650 l sec^{-1} . This high speed of pumping was necessary to cope with the inlet flow of gases (inert and reactive) at the operating pressure (10×10^{-3} Torr to 6.5×10^{-2} Torr).

The rotary pump had an ultimate vacuum of 3×10^{-2} Torr, and the combined use of the rotary and the diffusion pump produced pressures of the order of 5×10^{-4} Torr. Pressures down to 1×10^{-3} Torr were recorded by a Pirani gauge, the head of which was located on the top of the vacuum chamber, and pressures of 10^{-2} to 10^{-5} Torr were recorded by a Penning gauge, the head of which was located in the throttle, as shown in Fig. 10. With the baffle plate operating this did not give an accurate reading of chamber pressure, and was thus only used for estimates of the lower pressures during the preliminary stage of evacuation before the main stage of plating. During plating, pressures were recorded by the Pirani gauge.

It should be noted that pressure measurement with the use of Pirani heads was imprecise because of contamination of the gauge filament by the reaction gases. Approximately every 50 hours of deposition time the gauge was changed. Ultimately, the system was controlled by means of discharge current readings rather than by pressure readings.

Finally, the pump system was assisted by a liquid-nitrogen-cooled trap, which was located in between the butterfly valve and the mercury pump, in order to prevent the migration of backstreaming vapours from the diffusion pump into the chamber. The low temperature of this trap also reduced pumpdown time considerably. A continuous high speed system is necessary during chemical ion plating to prevent recontamination of the surface by sputtered impurities.

4.3 The Electrical Circuits and High Tension Supply

A stable, controllable, electrically safe d.c. power supply is required to provide the glow discharge. The glow discharge, as described in Chapter 2.3, transforms the electrical energy provided into kinetic energy of the species present in a vacuum chamber, and thus provides the energy needed for :-

- a) ionization of part of the species present and maintenance of the discharge
- b) heating of the substrate
- c) formation of the chemical compound by chemical synthesis which will create the coating of the specimen and
- d) good adhesion of the coating on the specimen surface

The high tension supply was provided by means of a regulated transformer and rectifier (Fig. 13) giving voltages varying from 0 to 5kV and currents of up to 250mA.

The use of voltages up to 5kV was necessary because, as mentioned in Chapter 2.3, the electrical field strength of the glow discharge is controlled by the applied voltage and the inter-electrode spacing. However, in the present work the inter-electrode spacing was kept constant, so to increase the field strength it was necessary to increase the applied voltage. Thus it was possible to use potential values which resulted in breakdown of the reactants, giving rise to ionization and activation of their molecules, which then interacted and created the titanium carbide coating. Finally, the use of high voltage values (4kV) proved to be beneficial to the adhesion of coatings onto the substrates. Potentials greater than 5kV are avoided to minimize the probability of X-ray emission, which may create

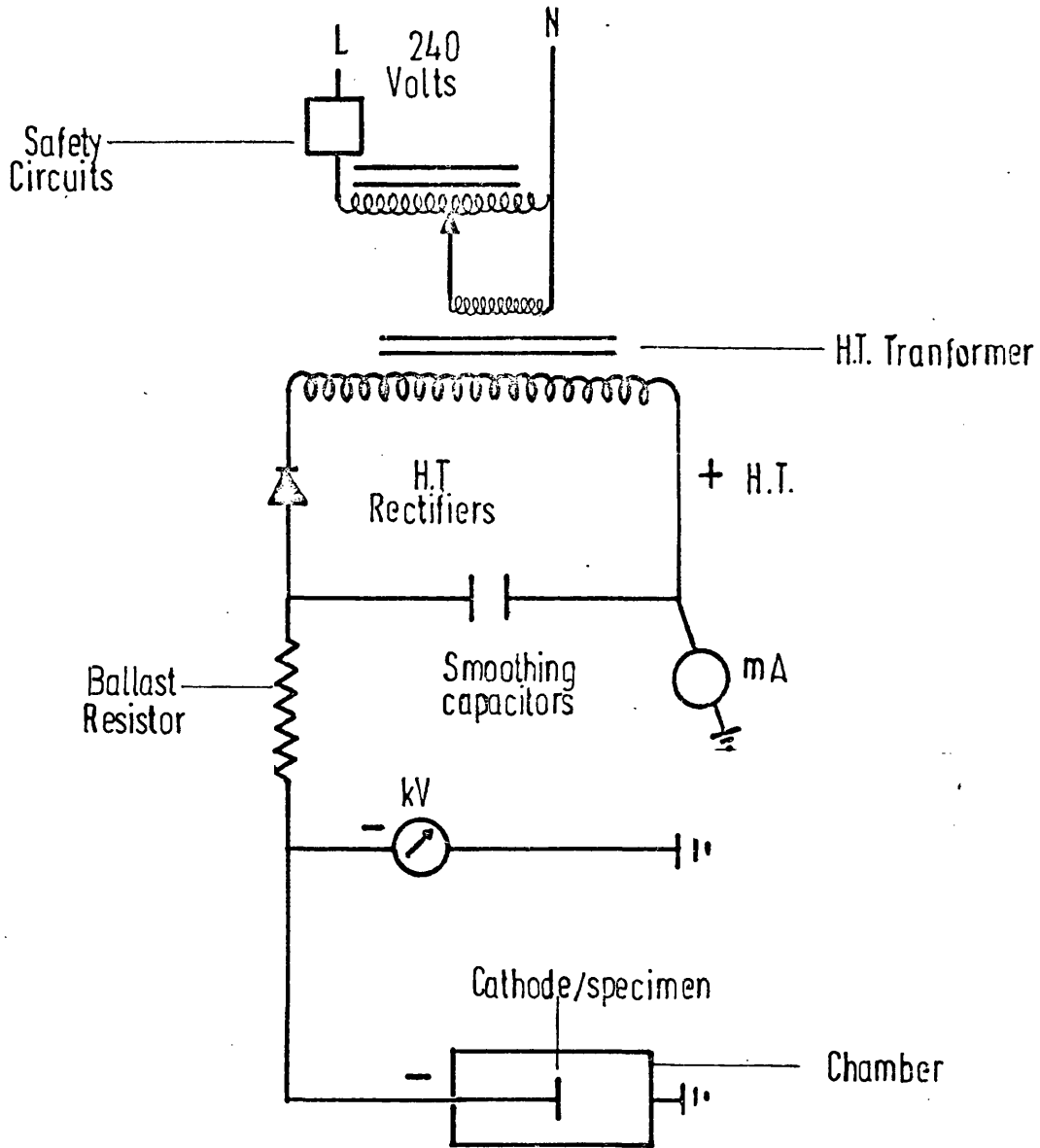


FIG. 13. Schematic diagram of electrical circuit
and High Tension supply.

dangerous conditions around the working area. Furthermore, potentials greater than 5kV are reported by Wan et al⁽⁵²⁾ to lead to higher rates of sputtering which is counterproductive to ion plating process and may be detrimental to the structure of the coating.

For reasons of safety the high tension supply was protected by comprehensive interlock circuit to guard against :-

- a) cooling water failure
- b) vacuum failure
- c) short circuit
- d) surge protection
- e) unauthorised interface

4.3.1 High Tension Lead Insultation-Cathode

The negative electrode or the cathode was originally placed on a vacuum-sealed current lead on the pedestal of the vacuum chamber. The original cathode was an aluminium disc of 130mm diameter and 6mm thickness, the under surface of which was surrounded by an earthed shield. With this arrangement the discharge was confined to the top surface of the cathode on which the mild steel specimens were placed. This led to minimal deposits.

This arrangement was abandoned and a single, smaller cathode-specimen was used connected to an extended H.T. lead. The extension lead was connected to the vacuum-sealed H.T. lead and insulated with Tufnol or Bakelite, and a final glass extension. Coatings were obtained, but deposition of coating material on the insulator caused short circuiting resulting in electrical breakdown of the insulator. In addition, the insulator was damaged by the increase in temperature

caused by its electrical breakdown. Such insulators had life times varying between 1 and 50 hours.

The cathode-specimen was a disc of 5.08cm diameter and 0.5cm height, cut from a standard sized bar of EN3B mild steel, and its edges were rounded to minimize the concentration of the electrical field⁽³⁾. The applied negative voltage caused the glow discharge to be struck between the earthed parts of the apparatus and the specimen itself.

With the above alterations the specimens obtained, examined from the aspects of appearance and surface morphology only, were not completely satisfactory because of the shadowing effect of different grounded metal supports and the walls of the chamber in the vicinity of the glow discharge. According to Putner et al⁽¹⁵⁾, the profile of the electric field across the cathode should be uniform in order to have homogeneous conditions of deposition over the whole surface of the cathode. Penetration of the dark space by grounded components will collapse the field and its symmetry will be distorted. The result of such interference was that the coating thickness varied from point to point. In order to avoid this problem all the redundant metallic components were removed from the chamber and the cathode-specimen was placed at its geometrical centre. Therefore the insulation-cathode holder was properly shaped in order to comply to these requirements.

The final design modification was the construction of a glass high tension lead insulation-cathode holder, shown in Fig. 14. In this arrangement the cathode-specimen was placed at the mid-point of

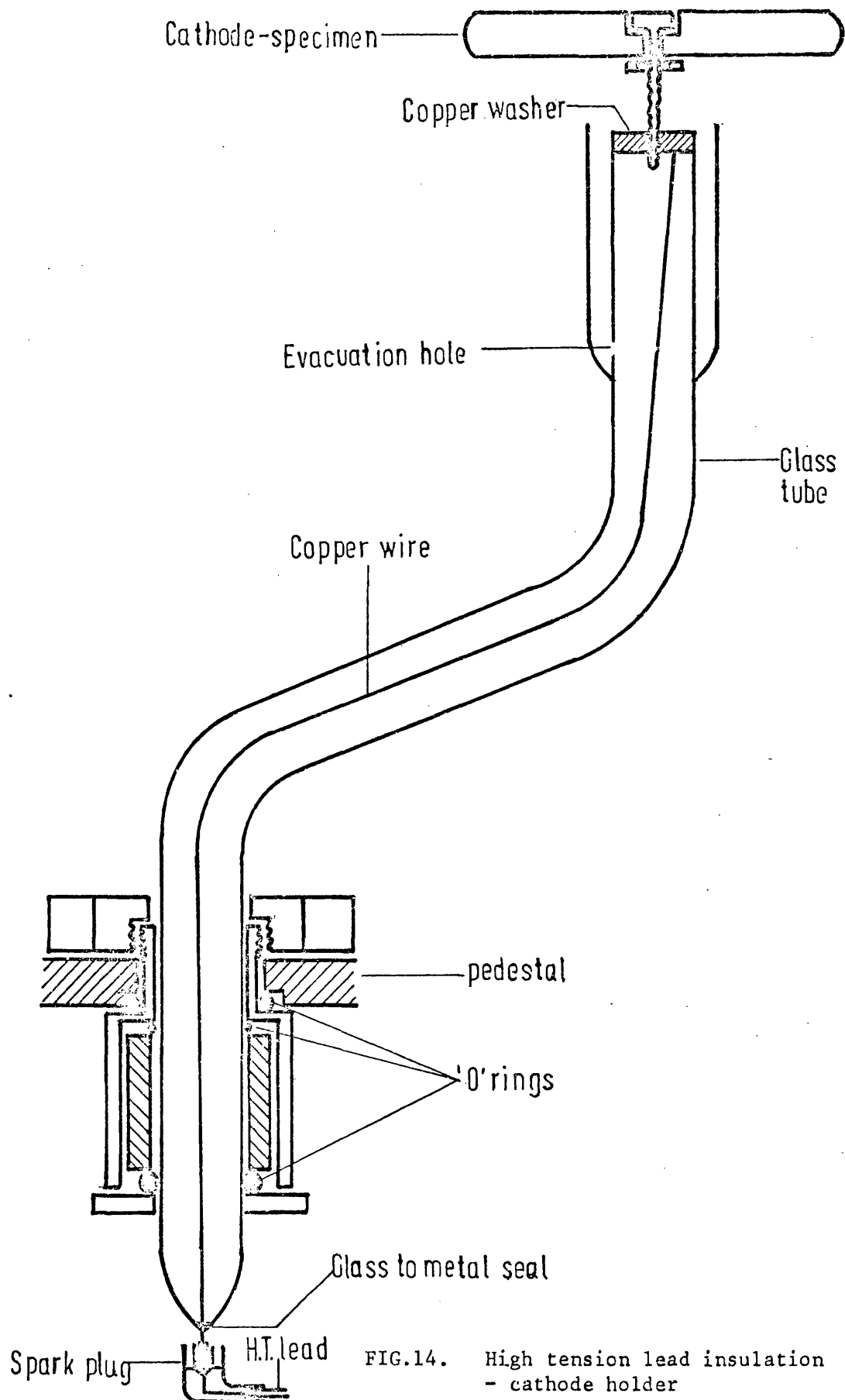


FIG.14. High tension lead insulation
- cathode holder

the chamber, so that both faces were participating equally in the process. This design proved completely satisfactory over periods of at least 100 hours operation.

4.4 Choice of Plating Materials

The materials which it is possible to use as reagents for any chemical ion plating application must satisfy the requirements of the method itself. Such requirements are :-

- a) the reagents must be sufficiently volatile to be passed into the reaction chamber as gases
- b) the chemical reaction must not occur until it is activated in the reaction vessel by the glow discharge
- c) it must be possible for the reagents under the conditions of glow discharge, to provide ions and so create and sustain the plasma state
- d) the reaction must proceed at a rate which gives coherent crystalline growth on the surface of the specimen

Transition metal refractory compounds, such as carbides, nitrides or borides, are the best candidates for chemical ion plating. Volatile compounds of the transition metals are relatively rare, and this is a limitation in chemical ion plating as it is for other methods, e.g. chemical vapour deposition. The most volatile compounds formed by refractory metals are the halides, e.g. tungsten hexafluoride, rhenium pentachloride⁽⁴⁵⁾. In table 2⁽¹³⁾ are listed volatile compounds of these metals which may be used in chemical ion plating as a source of the needed metal.

Most of these compounds can be transported readily at reduced pressure in heated pipework. If a coating such as a carbide is required, other reagents containing carbon are added: hydrocarbons such as methane, acetylene⁽⁹⁾, propylene⁽⁶⁹⁾ etc. are usually used.

For coatings as nitrides, ammonia or nitrogen may be used as sources of nitrogen^{(66),(70)}.

The introduction into the chamber of reagents such as titanium tetrachloride, which, under normal conditions of pressure and temperature is liquid, is achieved by passing a carrier gas through the heated liquid. Such carrier gases are generally inert ones. These inert gases serve the whole problem in different ways. Because they are chemically inert they carry the reactant vapour to the chamber without chemical alteration. They also play the role of agents of ionization, for the participating reagents and so sustain the gas discharge. Another and equally important role of the inert gases is the sputter cleaning of the specimen prior to deposition. As Stupp⁽²¹⁾ reported, the best and fastest sputter cleaning effect is obtained with the use of krypton. Generally, however, the high cost of krypton precludes its use. Lighter inert gases require higher pressures to maintain a discharge and give low cleaning rates. So argon was chosen because, apart from these reasons, it is readily available at reasonable cost.

During the first stages of the present investigation, the reagents used were the liquid titanium tetrachloride and methane. As carrier gas, argon was used. The titanium tetrachloride used was provided by BDH and is of minimum assay (ex.C1) 98,5%. The other gases used were of commercial grades.

The above combination of reagents satisfies the three first requirements listed at the start of this section, since they pass readily into the chamber, they do not react prior to their activation at relatively low temperatures and the argon carrier is capable of

sustaining the glow discharge alone. However, the fourth and most important requirement, that of creation of a coherent crystalline growth of titanium carbide on the surface of the substrate, was not achieved. The X-ray diffraction analysis showed that the coatings were amorphous or sometimes gave patterns matching titanium monoxide. These results were inconsistent and inconclusive from run to run. Analysis of coatings by EPMA showed the same kind of results and no definite stoichiometry between titanium and carbon. It was found that these films were titanium rich. By the same method in some cases films approximating to titanium dioxide in composition were formed. The titanium to carbon ratio was investigated more thoroughly, by varying the $\text{TiCl}_4/\text{CH}_4$ ratio in the feed, and was found that carbon could be deposited (and even then, slowly) when the concentration of titanium tetrachloride was very low. This may be due to the low reactivity of methane.

So, acetylene was substituted for methane. This is known to be less stable due to the carbon-carbon triple bond. Also the use of acetylene is advantageous compared to methane because the carbon content is higher. But even with acetylene and using low values of power density at the cathode as previously, the results obtained were not encouraging. The films obtained were amorphous according to X-ray diffraction analysis or they consisted of micro-crystalline titanium monoxide. Examination by electron probe micro-analysis led to similar conclusions. At this stage films obtained consisted of titanium, chlorine, oxygen and traces of carbon. It was difficult to decide whether the oxygen was incorporated into the coating during the deposition process, or after the exposure of the specimen to the atmosphere. However, the major question that arose was, why it was

possible to deposit titanium while at the same time carbon was not deposited. Either or both of the two following reasons may be responsible for the above behaviour. First, the hydrocarbon under the conditions of glow discharge is dissociated and ionized, as was confirmed by relevant experiment, see Fig. 17, but the carbon bearing ions were not deposited on the cathode. Second, the carbon was deposited but it was sputtered at much higher rate than titanium by the bombardment of heavy argon ions.

So, hydrogen was substituted for argon, as the carrier gas. Hydrogen atoms being much lighter than those of argon atoms, it was hoped that the sputtering effect of carbon atoms could be minimized. A second obvious effect was that the reducing atmosphere of hydrogen in the chamber would prevent oxidation of the coating during the deposition process. A third reason was that hydrogen was required by the stoichiometry of the reaction involving acetylene. Hydrogen is claimed to be beneficial by Elyntin et al⁽³³⁾, accelerating the titanium carbide formation process due to the increase in the amount of carbon formed by decomposition of the carbonaceous gas. Furthermore the use of hydrogen eliminated the problem of blocking of the needle valve. However, the results on film formation were still rather poor. They were showing deficiency in carbon and oxygen was still present. The adhesion of these films was poor because of the formation of gas bubbles of 1 - 5 μ m in diameter. Peeling of the film started from these bubbles within two to three days. So finally the carrier gas was changed again to a mixture of argon with 5% hydrogen. The aim was to prevent blocking of the needle valve and to give good adhesion. Eventually this proved to be the best carrier gas.

Mearns⁽⁷⁾ observes that metallic films can be deposited from carbonyls and other organometallic compounds. To investigate this, a series of experiments were carried out using tetra-isopropoxy titanium. This contains its own internal source of carbon and titanium (though it does also contain oxygen). This substitutes the combination of titanium tetrachloride and hydrocarbon. Film formation proceeded at low rates and only on anodic areas. Generally the obtained results were not encouraging so the method was abandoned.

Having tried all the above combination of reactants it was obvious that in order to achieve the required result, that of obtaining titanium carbide coatings, the other parameters of ion plating had to be investigated. Since the other parameters such as (a) pressure of the discharge, (b) substrate voltage, (c) composition of the gases present, (d) substrate geometry, had already been investigated the only factor remaining was to investigate the influence of the current for given values of the other parameters. Finally this was proved to be the vital factor for the deposition of titanium carbide coatings.

CHAPTER 5

EXPERIMENTAL AND ANALYTICAL WORK

5.1 Selection of Operational Parameters

The first experimental stages were concerned with the finding of the operational conditions of the apparatus. The most suitable carrier gas proved to be argon plus 5% hydrogen. It was found, as expected from literature^{(15),(18)}, that the current of the discharge is a function of the applied potential and the pressure of the chamber. These can be seen in Table 4 and graph (Fig. 15). The current flowing during a discharge, under constant potential and pressure, is constant provided that the clearance between cathode and the anodic parts of the chamber is greater than the cathode dark space, because if this becomes smaller the discharge extinguishes. For a given constant clearance between cathode and the anodic parts of the chamber, and for a given potential it was found that the current was very sensitive to pressure changes. Thus changes in pressure which were hardly recorded on the Pirani gauge, i.e. smaller increments than 1×10^{-3} Torr gave current changes in the order of 10mA. Provided that the feed of gas reactants was kept constant (as indicated by constant flowmeter and manometer readings) the discharge current was corrected by the use of the baffle plate acting as a very fine control device. However, because of partial blocking of the needle, indicated by increased manometer reading, adjustment of this valve to maintain constant conditions was necessary at about 30 min. intervals. In order to have stable plating conditions during a run the following

TABLE 4. Current of glow discharge in argon versus voltage for different chamber pressures (cathode area = 132, 5 cm²)

Pressure of Chamber x 10 ⁻³ Torr	Voltage kV	Current mA
10	0.4	0
10	0.8	10
10	1.1	20
10	1.2	30
10	1.4	40
8	0.6	0
8	1.2	10
8	1.5	20
8	1.8	30
8	2.0	40
6	0.8	0
6	1.5	10
6	1.9	20
6	2.1	30
6	2.4	40
4	0.9	0
4	1.9	10
4	2.3	20
4	2.7	30
4	3.0	40

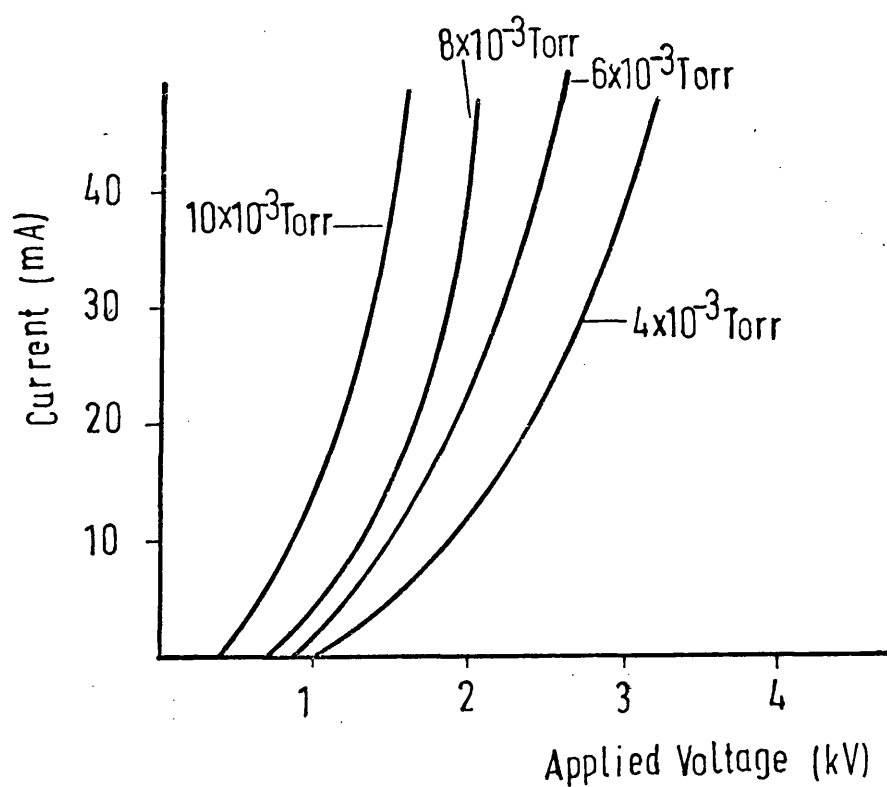
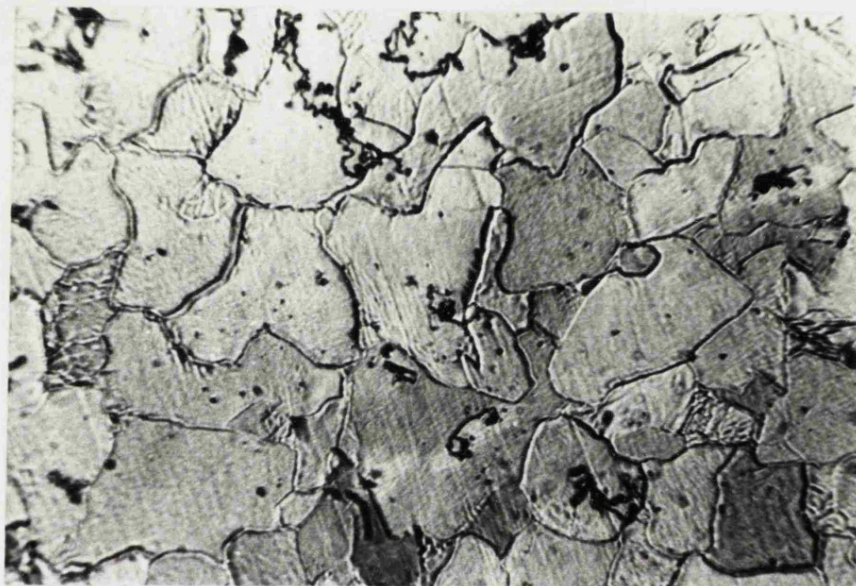


FIG. 15. Applied voltage potential and current for different pressures during an Argon glow discharge in the apparatus of Figure 10.

precautions were taken. The chamber was evacuated to pressures of about 10^{-4} Torr. The cold trap of solid carbon dioxide-methanol was charged, the thermostat of water bath, and the heating tape of the hose connecting the bubbler with the needle valve (2), were turned on. Another interim step which was taken, was to evacuate the wash bottle itself and the whole bubbler line, up to the needle valve(1) (Fig. 12) to a pressure 300 - 400 Torr so that the pressure before and after the by-pass valve adjustment, was as stable as possible thus insuring an undisturbed transition from the sputter cleaning stage to the actual deposition stage. This transition period proved to be of maximum importance because when it was not even, it was observed that spalling of the coating could take place, at the central region of the upper surface of the specimen, during or after the deposition, as described in Chapter 6.2. After these precautions, then the inert gas was admitted to the chamber at a predetermined flow rate. The system was allowed to reach a steady state and then the potential was applied and adjusted to the preselected value. With the application of the potential the discharge was formed, thus sputter cleaning began. Generally when sputtering started the initial current was unstable and some arcing took place an effect which is also reported by Spalvins⁽⁵³⁾, Holland⁽⁷⁾ and others. In order to obtain, under a given voltage, the desired current the baffle plate was used as a fine control of the pressure on which the current depends. Having stabilized the current the sputter etching or cleaning of the surface of the specimen was then continued until the surface was cleaned of oxide layers and was free of skin effects of cold working which were produced with mechanical polishing. During this stage of sputter cleaning of the specimen, the discharge current gradually

decreased, so every so often the position of baffle plate had to be adjusted in order to keep the current stable at the wanted value. Usually after about 30 min. the current stabilized and no further adjustment was necessary. This was an indication that the sputter cleaning was completed, because the metal oxides, which as Mattox⁽⁹⁾ reports, having higher secondary electron emission coefficient than the metals were removed, exposing the clean metal surface which provides constant electron emission and thus constant current. Then further 5 min. were usually allowed to assure that the discharge current was not decreasing any further. Microscopical examination of the surface of specimens prepared to investigate the influence of the ion bombardment showed that after 35 min. of sputtering they had been deeply etched revealing the complete grain boundary pattern of the mild steel substrate used. It is known that a newly polished metal surface starts oxidizing from the grain boundaries, so since these boundaries were revealed and this proceeded in depth under vacuum conditions by ion bombardment, it means that all the possible iron oxides had been sputtered. Picture of Fig. 16 shows a sputter etched steel substrate, under the conditions of 4kV voltage, and 200mA current, and time 35 min. Furthermore the results of good adhesion of coatings obtained proved that the 35 min. period was sufficient for sputter cleaning.

When the sputter cleaning finished then the reactants were admitted into the chamber. First the titanium tetrachloride was allowed to enter by adjusting the by-pass valves of the bubbler. By this adjustment the carrier stream was led through the heated wash bottle. The entrance of this reactant was associated with a change in hue of the discharge. The colour of the argon discharge alone was



— 17 μ m

Fig. 16 Sputter etched mild steel substrate in argon glow discharge under the conditions: voltage 4kV, current 200 mA, time 35 min.

bluish and the titanium tetrachloride presence, turned it to a pinkish one. Finally, when the discharge was stabilized again (stability of current) which was done in less than one min., then the other reactant acetylene was admitted. Immediately the hue of the discharge changed again to a dull reddish colour. The entrance of the acetylene caused an increase in the discharge current, first due to the chamber pressure increase and second due to its greater electrical conductivity than the other gases present. This can be deduced from the graph (Fig. 17). Finally the current was adjusted to the desired value. From this stage onwards the discharge was maintained until the desired film thickness was obtained. It should be noted that as the deposition progressed the colour of the discharge changed and its luminosity became duller and duller and approximately after 3 - 3,5 hours the discharge was limited to a goldish colour sheath of glow around the cathode. During the whole process the current remained constant even when the discharge luminosity decreased to a very low level.

Another effect which sometimes was noticed, was an arcing effect taking place on the specimen surface. This was observed whenever spalling of the coating occurred during the deposition period as a result of poor adhesion. This was due to the re-contamination of the surface of the substrate whenever the transition from the cleaning to actual deposition process was not even. The reason that at certain times the transition was not even, was because the needle valve that used to regulate the flow rate of argon, partially blocked when first exposed to vapours of titanium tetrachloride. In such a case in order to keep the flow rate constant the valve had to be opened further. However, as soon as the valve was opened the cause of blocking was eliminated and

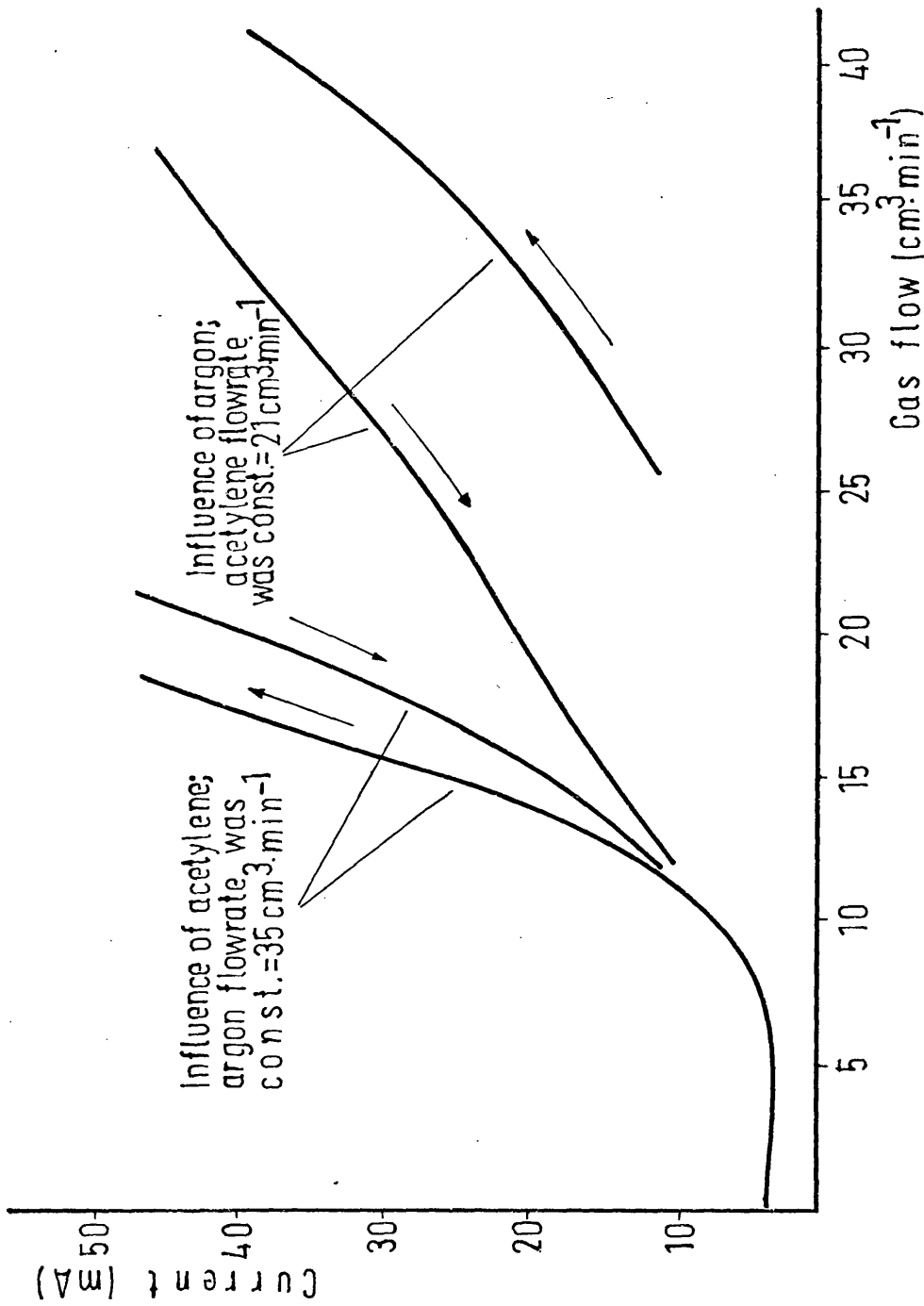


FIG. 17. Glow discharge current changes as a function of the gas flows when the applied voltage was 4kV.

the flow rate was suddenly increased in current, giving a glow-to-arc discharge transition, an effect which is reported by Howatson⁽¹⁷⁾.

As soon as this effect occurred the discharge was switched off to avoid any damage to the electrical instruments, the needle valve was partially closed and the baffle plate was then opened in order to increase the rate of pumping. When the pressure had reached the required low value, the discharge was again reactivated and the needle valve was adjusted to give the wanted flow. However, sometimes the time required to reach the low pressure was up to 5 min. and during this period the surface that had been cleaned by ion bombardment was recontaminated by the residual gases, resulting in poor adhesion between the coating and the substrate, and eventually spalling off of the coating.

Whenever spalling occurred during deposition, fragments of the coating detached, could be seen standing vertically on the surface following the electrical field lines. Possibly these fragments were acting as electrical charge accumulators due to high field concentration and were the cause of arcing.

The maximum amount of titanium tetrachloride that could enter the chamber was governed by its saturated vapour pressure⁽⁷¹⁾. This pressure is given by :-

$$\log p = \left(- \frac{0.2185A}{T} \right) + B$$

where T, the absolute temperature in degrees of Kelvin, p the partial of the reactant vapours in Torr, A is the molar heat of vapourization in calories per gram mol which for titanium tetrachloride is equal to 9,292.2, and B is a constant which for the same reactant is equal to 7.883. Using the above equation the maximum partial pressure of titanium

tetrachloride at 60°C was calculated as 61.075 Torr. Knowing the flow rates of the carrier gas the maximum mass flow rates of entering titanium tetrachloride is shown in Table 5. These mass flow rates could correspond to vapourization of 9.7g. to 13.0g. of titanium tetrachloride over a period of a run (3h.10min.), when the carrier gas flow rate is between $38.20 \text{ cm}^3 \text{ min}^{-1}$ and $51.30 \text{ cm}^3 \text{ min}^{-1}$, respectively. However, such vapourization rates were not observed in practice indicating that the vapour stream was not saturated.

The whole series of experiments, after the successful deposition of titanium carbide, were carried out under the conditions given below :-

Voltage:	3 - 5kV
Current:	80 - 240mA
Chamber Pressures:	1×10^{-3} - 6×10^{-2} Torr
Water bath temperature:	60°C

The specimens used were located on the high tension lead through, thus acted as the cathode of the system, (Fig. 14). Because the specimens were placed at the geometrical centre of the chamber, without any shielding by neighbouring bodies, the electrical field on the flat surfaces was homogeneous. The only shielding effect was displayed near the glass insulator on the high tension lead through. Thus the whole specimen surface was exposed to a nearly uniform electrical field and so the created coating had uniform thickness within 10% variation, all over the specimen surface, except only at the connecting point. At that point and around it at a radius of approximately one centimeter, even the nature of the obtained coatings was different (softer) than that of the rest of the surface, and usually was detached in form of flakes. Because both gas streams entered at the top of the

TABLE 5. The maximum mass flowrate of titanium tetrachloride that could enter the chamber when the water bath temperature is 60°C.

Carbonaceous Gas % in Reaction Mixture	Flow Rate $\text{cm}^3\text{min}^{-1}$ at 760 Torr, 25°C A + 5% H_2	Mass Flow Rate mg min^{-1} of TiCl_4
6	51.30	68.90
9	49.70	66.70
12	48.00	64.50
15	46.00	62.10
18	44.80	60.00
21	43.10	58.00
24	41.50	56.00
27	39.80	53.40
30	38.20	51.20

chamber, nearly 25cm from the cathode, then adequate mixing by gas scattering was ensured.

Thus both surfaces were exposed to almost identical conditions, in contrast to those obtained in conventional and reactive ion plating. This was because there was not any high flux of evaporating coating material onto the one or the other surface as happens in the other ion plating methods.

Another parameter which played an important role in the present work was temperature. At an early stage of the present investigation incorporation of a thermocouple into coating chamber was tried, but it was abandoned for two reasons. First safety and second distortion of the glow discharge electrical field. Safety problems arose with the electrical insulation of the measuring circuit. The distortion of the discharge electrical field was more important because of creation of uneven coatings around the point of the contact of the thermocouple with the specimen-cathode. This was due to concentration of electrical field lines around that point resulting in higher degree of sputtering than the rest of specimen surface. In addition, deposition of conducting material on the thermocouple insulation led to further distortion of the field and eventual short circuiting. However, temperatures of 240°C were recorded with the following conditions of depositions: current 40mA, voltage 4kV and deposition time 4 hours.

The temperature increase depends upon the number and the energy of the ions, in other words upon the current and the voltage of the discharge. It was observed that a voltage of 4kV and current 200mA after a period of 10 - 15 min. raised the temperature of the specimen

to just visible red hue, while an extension of the bombarding time under the same conditions produced no change to the colour of the specimen and hence no change to its temperature. An optical pyrometer was used to measure its temperature, but because this was below the low limit of the instrument scale, which was 700°C , no measurement was recorded.

To find out the temperature range of the substrate the following experiment was carried out. On a usual mild steel specimen-cathode small pieces of the following elements were placed (the numbers in parenthesis are their melting points in $^{\circ}\text{C}$): zinc (419), antimony (630), aluminium (660), barium (725), calcium (839). The discharge was established in presence of argon + 5% hydrogen, i.e. (the carrier gas used in the whole series of the experiments), the applied voltage was 4kV, the current 200mA and the time 35 min. In 10 min. time after the start of the discharge the zinc started melting. This was sensed due to the change of the discharge hue and also the change of shape of the zinc piece. However, none of the other elements melted during the 35 min. run. The conclusion from this experiment was that the temperature of the cathode was above 419°C , but below 630°C .

So since the discharge conditions used for depositing the titanium carbide coatings were the same as in the above experiment it can be inferred that the substrate temperature during the deposition was in this range, in which the needed activation energy, according to thermodynamic calculations (Appendix I), of the reaction taking place could be provided.

After X-ray and other evidence showed that titanium carbide coatings had been formed then investigations of the influence of different operational parameters on the nature and properties of the coatings were carried out. One series of experiments was carried out to find the influence of current when all the other variables were kept constant. Table 6 shows the details of this series of experiments.

TABLE 6. Conditions used to investigate the influence of discharge current on coatings

C ₂ H ₂ (%) by Volume	Voltage (kV)	Current (mA)	Pressure Torr x. 10 ⁻³	Flow cm ³ min ⁻¹ at 760 Torr, 25°C		Deposition Time Hours Min	
				A+5%H ₂	C ₂ H ₂		
30	4	240	49	38.2	16.4	3	10
"	"	200	42	"	"	"	"
"	"	160	38	"	"	"	"
"	"	120	35	"	"	"	"
"	"	100	38	"	"	"	"
"	"	80	37	"	"	"	"

Another series of experiments was carried out to investigate the influence of the composition of the gas reactants. The current of 200mA was chosen because from the first series of experiments it was found that using this current good crystalline titanium carbide deposits were formed. Table 7 shows the details of this series of experiments.

TABLE 7. Conditions used to investigate the influence of composition of the gas reactants on coatings

C ₂ H ₂ (%) by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm ³ min ⁻¹ at 760 Torr, 25°C		Deposition time hours min	
				A + 5%H ₂	C ₂ H ₂		
6	4	200	46	51.3	3.3	3	10
9	"	"	45	49.7	4.9	"	"
12	"	"	48	48.0	6.6	"	"
15	"	"	46	46.4	8.2	"	"
18	"	"	45	44.8	9.8	"	"
21	"	"	48	43.1	11.5	"	"
24	"	"	49	41.5	13.1	"	"
27	"	"	47	39.8	14.7	"	"
30	"	"	48	38.2	16.4	"	"

The influence of voltage was investigated with three experiments, the details of which are given on Table 8.

TABLE 8. Conditions used to investigate the influence of voltage on coatings

C ₂ H ₂ (%) by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm ³ min ⁻¹ at 760 Torr, 25°C		Deposition Time Hours Min	
				A + 5%H ₂	C ₂ H ₂		
21	3	200	69	43.1	11.5	3	10
"	4	"	48	"	"	"	"
"	5	"	43	"	"	"	"

The influence of time dependance on the thickness of the coatings was studied as well, the details of this series of experiment are given on Table 9.

TABLE 9. Conditions used to investigate the film thickness as a functions of time

C ₂ H ₂ by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm ³ min ⁻¹ at 760 Torr, 25°C		Deposition time Hours Min	
				A + 5%H ₂	C ₂ H ₂		
30	4	200	35	38.2	16.4	4	15
"	"	"	38	"	"	3	12
"	"	"	37	"	"	2	08
"	"	"	38	"	"	1	04

The influence of the nature of the substrate was studied to find out how the adhesion of the coating is affected. The alternative substrates used were carburized steel discs of the same dimensions as the others used in the other series of experiments. The treatment followed for the preparation of such substrates was as follows: well polished mild steel substrates were carburized by the pack carburizing method at 950°C for 10 hours. After that the furnace was allowed to cool down at room temperature. Then followed reheating of samples for half-an-hour at the same temperature and subsequently they were quenched first in brine and then in the freezing mixture of solid carbon dioxide-methanol (-72°C). The object of these processes was to transform the structure of the mild steel to a fully martensitic one, thus enhancing its hardness. The hardness of these substrates measured was 950VHN. Finally these substrates were polished again, prior to their exposure in the coating chamber. The conditions of the deposition followed of these specimens are given on Table 10.

TABLE 10. Conditions used to deposit coatings on carburized steel substrates

C ₂ H ₂ (%) by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm min ⁻¹ at 760 Torr, 25°C		Deposition time Hours Min	
				A + 5%H ₂	C ₂ H ₂		
9	4	200	45	49.7	4.9	3	10
21	"	"	49	43.1	11.5	"	"

To find out where the formation of titanium carbide begins on the surface of the substrate and also in order to see how the coating covers the substrate at the first stages of deposition three experiments were carried out. The deposition time was 5, 10 and 20 min. Table 11 shows the conditions of deposition used.

TABLE 11. Conditions used to study how the coating covers the substrate at the first stages of deposition

C ₂ H ₂ by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm min ⁻¹ at 760 Torr, 25°C		Deposition Time Min
				A + 5%H ₂	C ₂ H ₂	
30	4	200	38	38.2	16.4	5
"	"	"	"	"	"	10
"	"	"	"	"	"	20

Another series of experiments carried out with the intention of finding the friction coefficient of titanium carbide coatings against a stainless steel counterface. The samples used in this case were small mild steel discs of 1.25cm in diameter and 0.6cm in height. Six samples of such discs were placed on the upper surface of the usual 5.08cm diameter cathode-specimen, at the apices of a regular hexagon which was formed by milling suitably sized recesses on the surface of the cathode. The samples were protruding nearly 0.3cm above the cathode

surface. The conditions used for this series of experiments are shown on Table 12. The deposition time was not kept constant due to apparatus malfunction.

TABLE 12. Conditions used to coat samples for coefficient of friction measurements

C ₂ H ₂ (%) by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm ³ min ⁻¹ at 760 Torr, 25°C		Deposition time Hours Min	
				A + 5%H ₂	C ₂ H ₂		
9	4	200	4	49.7	4.9	3	10
15	4	200	4	46.4	8.2	2	10
21	4	200	45	43.1	11.5	1	
30	4	200	47	38.2	16.4	3	10

Other minor series of experiments were as follows :-

- a) A sample of 7cm diameter was used under the conditions of Table 13(a) which reduces the current density by 48%.
- b) A period of 30 min. deposition with titanium coating only (absence of acetylene) was interposed between the sputter cleaning period and the actual deposition period of titanium carbide in presence of both reactants, which was intended to create a graded coating.
- c) The influence on the adhesion in the case where the deposition started directly without any prior sputter cleaning was investigated.
- d) The "throwing power" of the method was investigated with two different experiments. The first one was carried out on a usual specimen-cathode which was perforated with through or blind holes of different diameters. The second was carried out with a different arrangement of substrate which consisted with three cylindrical specimens which were placed normal to the surface of the cathode on the apices of

an equilateral triangle. Provision was taken so that the total area of this arrangement was equal to the area of a usually used substrate, thus keeping a constant current density.

e) The ability to obtain a coating of metallic titanium was investigated by using only titanium tetrachloride in absence of acetylene through out the deposition period.

Table 13 shows the conditions under which these experiments were carried out.

TABLE 13. Conditions used to investigate the influence of different minor parameters on coatings

C ₂ H ₂ (%) by Volume	Voltage (kV)	Current (mA)	Pressure Torr x 10 ⁻³	Flow cm ³ min ⁻¹ at 760 Torr, 25°C		Deposition Time	
				A + 5%H ₂	C ₂ H ₂	Hours	Min
a) 30	4	200	40	38.2	16.4	3	10
b) "	"	"	46	38.2	-	-	30
c) "	"	"	"	"	16.4	3	10
d ₁) 21	"	"	"	"	"	4	-
d ₂) 30	"	"	49	43.1	11.5	3	10
e) 0	"	"	38	38.2	16.4	3	10
	"	"	28	32	-	3	30

All deposition periods were followed by a 45min period of cooling which took place in the presence of the carrier gas. After that the specimens were exposed to the atmosphere. Sometimes it could be seen that the coatings, mainly prepared from gas reaction mixtures containing 18% to 30% C₂H₂, were already spalled off at points around the centre of the specimen. However, even when the coating was intact it was found that at the first hours after its removal from the chamber the specimen should not be touched because sometimes it spontaneously failed by delaminating immediately upon handling. It was found that a

period of time of 24 hours was sufficient before any cutting could be started for examinations and measurements. From this it can be inferred that during this period an aging mechanism was taking place. The same effect was noticed by Mukherjee et al⁽²⁹⁾ when they had deposited titanium carbide on carburized steel substrates by the sputtering technique. In order to explain this aging effect they report that "Diffusion of oxygen to the interface from the film surface and the formation of intermetallic compounds at the interface have been suggested to explain similar aging phenomena in deposited films. However, we feel that the improvement in adhesion which occurred during aging of the present samples resulted from short-range-diffusion relieving interfacial stresses due to differential thermal contraction and lattice mismatch". It seems that the same mechanism determines the aging effect also in the cases of the chemical ion plating coatings. The structure and properties of coatings obtained was studied by a number of techniques.

5.2.1 Examination by X-ray Diffraction

As has already been mentioned working at conditions of low currents (40mA) the obtained coatings were always amorphous to X-rays, however electron probe microanalysis still showed the presence of titanium and carbon. By increasing the current to 200mA, under the same conditions of applied voltage (4kV) and the same composition of gas reactants (30% acetylene) coatings were repeatedly obtained which indicated by X-ray diffraction that crystalline titanium carbide has been formed.

Thus it was necessary to find the current value at which the carbide became fully crystalline. A series of experiments under the same conditions of applied voltage (4kV), gas composition (30% acetylene) and time (3 hours 10 min) was carried out. The currents used were 80, 100, 120, 160, 200 and 240mA. The coatings obtained in this series of experiments always gave some spalled off fragments which were used for X-ray diffraction powder analysis. The results of this analysis showed that the coatings obtained had a more definite diffraction pattern as the current increases. Fig. 18 shows the smoothed microdensitometer traces of the Debye-Sherrer films produced. At 80mA there are no lines on the X-ray diffraction pattern, an indication of the "amorphous" state of deposited material. At 100mA the lines corresponding to the planes $\{111\}$, $\{200\}$ and $\{220\}$ are present but they are very faint. At 120mA the same lines are present but they seem to be more intense than those of the corresponding of 100mA. At 160mA besides the lines of the mentioned planes also the line of the plane $\{311\}$ is present. At the same time the intensity of lines is higher than previously.

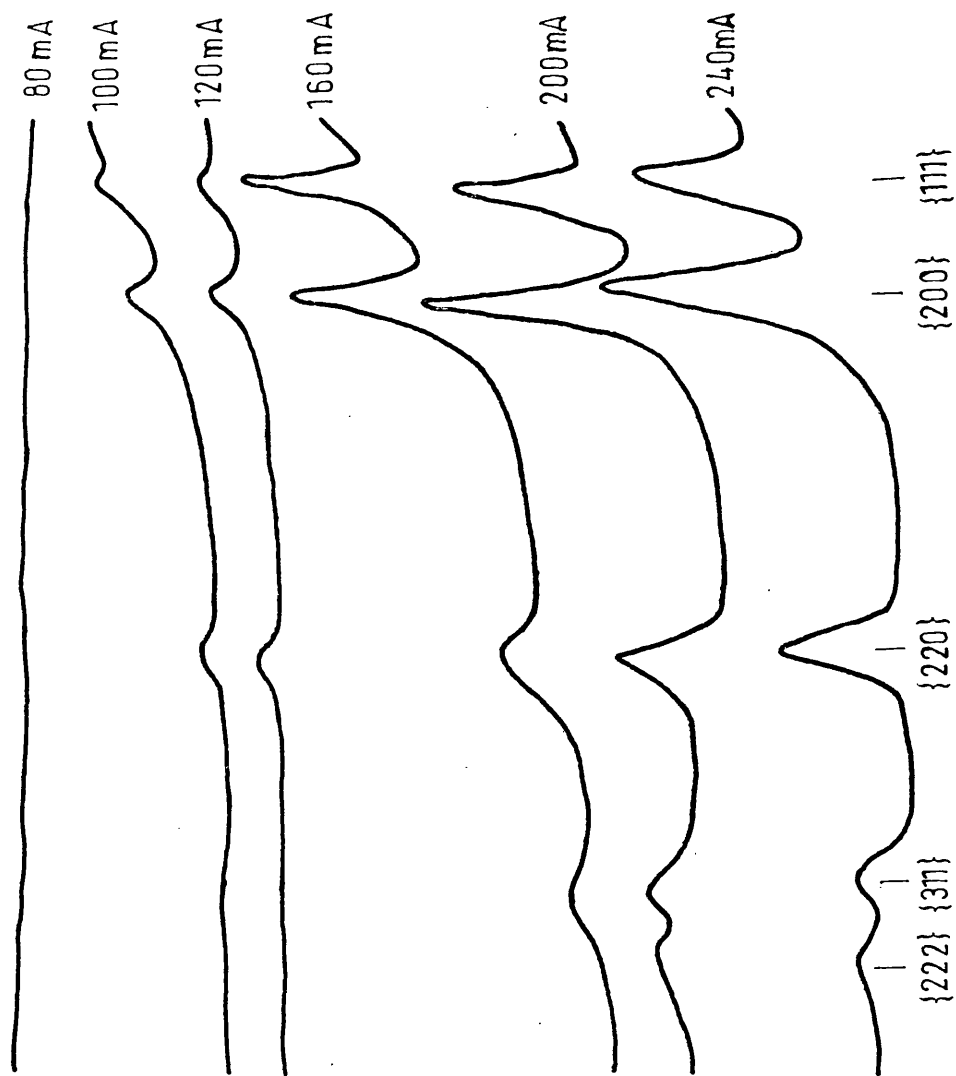


FIG.18. Smoothed microdensitometer traces of Debye-Scherrer films of coatings produced at different currents.

Finally at 200mA and 240mA the line of the plane $\{222\}$ appears and the intensity of all lines present is much higher than in the forementioned cases. It is worth noticing that the order of appearance of these lines correspond to the order of intensity of the lines listed on the ASTM card for titanium carbide.

In an attempt to find if the degree of crystallinity changes under the above conditions, the optical density of the lines corresponding to planes $\{111\}$ and $\{200\}$ of each film were measured with the use of the microdensitometer (Joyce Loebel MkIIIc). The results of this experiment are tabulated on Table 14. From these it can be seen that the intensity of the lines increase as the current does. But the peak width at half height does not change significantly with current. From this it can be said that the change in the X-ray intensity is not due to increased grain size, though the number of titanium carbide crystals in the X-ray sample must be increased due to the increase of coating thickness. The conclusions from this series of experiments is that the more definite diffraction pattern is obtained at high current values (200 and 240mA). Taking this into account and also that the discharge operates better (stable) at currents of 200mA, the whole series of the following experiments were carried out at this current.

As noted in Chapter 5.1 the coatings obtained from gas reaction mixtures containing between 18% and 30% acetylene were partially spalled during the cooling period or during the first hours after their removal from the coating chamber. The spalling effect was displayed by fragmentation of the coating into small sized fragments.

TABLE 14. Intensity and peak width at half height for the Debye-Scherrer film lines corresponding to the planes {111} and {200} of titanium carbide deposited at different glow discharge currents.

Discharge Current mA	Coating Thickness μm	Intensity (arbitrary units) for the plane		Peak width at half height (arbitrary units)	
		{111}	{200}	{111}	{200}
80	4.70	0	0	0	0
100	2.85	0.40	0.40	0.75	0.85
120	3.25	0.50	0.55	0.85	0.90
160	8.50	1.50	1.70	0.60	0.75
200	13.60	1.65	2.30	0.90	1.00
240	-	1.80	2.70	1.10	1.25

Some of the fragmented material was directly used for X-ray diffraction powder analysis without any other interim preparation (e.g. grinding in pestle and mortar). Each sample, for X-ray powder analysis, was mounted onto a 80 μ m lead free glass fibre using silicone grease as the adhesive. The glass fibre was mounted on a Philips type PW1010 X-ray diffraction unit. Powder diffraction patterns were photographed using a 114.83mm diameter, Debye-Scherrer camera with a Straumanis film mounting using nickel-filtered copper radiation for 6 hours.

The coatings obtained from reaction mixtures containing less than 18% acetylene, did not spall and so it was difficult to use the powder technique for X-ray diffraction analysis. Instead, the diffractometer method was used. The samples prepared were rectangular pieces (1.30cm x 1.80cm) cut from the coated specimen and were mounted in a Philips powder diffractometer (type PW1030 goniometer, PW4620 channel analyser and PW1965 Xenon proportional counter), using copper radiation. On the charts obtained only the peaks corresponding to the first three planes $\{111\}$, $\{200\}$ and $\{220\}$ of titanium carbide could be seen. Also due to the fact that these coatings were thin (5.5 μ m to 10 μ m) peaks corresponding to planes of α -iron were recorded. Because the coatings deposited on the martensitic steel substrates were also adhered well, they were analysed by the same method. The pattern of lines on the Debye-Scherrer films and on the diffractometer charts was characteristic of the face centred cubic structure and the lattice constants calculated are given on Table 15. Typical films are given in Fig. 19.

TABLE 15. Lattice constant measurements of titanium carbide coatings deposited under different conditions.

Specimen-cathode	Volt. (kV)	C ₂ H ₂ % in gas reaction mixture	Weight% of carbon in coating by EPMA	Lattice constant(Å)	
				Method used	
				Debye- Scherrer	Diffraction meter
Mild Steel	4	6	37.70		4.320±0.011
" "	4	9	37.80		4.352±0.013
" "	4	12	43.40		4.346±0.006
" "	4	15	52.94		4.347±0.005
" "	4	18	52.87	4.355±0.016	
" "	4	21	61.40	4.351±0.014	
" "	4	24	67.40	4.353±0.007	
" "	4	27	64.82	4.352±0.011	
" "	4	30	61.30	4.336±0.025	
" "	4	30	-	4.366±0.028	
" "	4	30	65.10	4.355±0.010	
Carburized Steel	4	9	-		4.341±0.019
" "	4	21	-		4.371±0.007
Mild Steel	3	21	-	4.343±0.018	
" "	5	21	-	4.346±0.021	
Mild Steel*	4	30	-	4.354±0.027	

*Current density on the substrate reduced by 48%, using a bigger surface specimen.



FIG.19. Typical Debye-Scherrer films of titanium carbide coatings obtained.

The X-ray diffraction films obtained by the powder technique had a background blackening effect, except in the case of amorphous or low crystallinity coatings, due to fluorescence radiation from the iron atoms present in the coatings. The presence of the iron atoms can be explained as a result of sputtering of the surface layer in an atomic scale at the first stages of deposition, up to the point of complete covering of the steel substrate. These sputtered iron atoms entering into the plasma region are ionized, back-scattered and codeposited on the substrate with the other coating elements as the deposition proceeds. It has been noted that the fluorescence effect is more prominent as the material shows a more definite diffraction pattern. It could be seen that the X-ray diffraction film corresponding at 80mA is free of any fluorescence effect while that one corresponding at 240mA has the maximum background blackening of the whole series of films. The other films deposited at intermediate current values have a background blackening effect lying in between the limiting cases. A possible explanation of the presence of iron atoms in a different degree as the current of the discharge increases, is that the sputtering rate of iron atoms increases as the discharge current does. This was confirmed by the greater sputter etching effect of steel substrates as the glow discharge current increases.

Rudy⁽⁷²⁾ reports a background blackening effect (using Cu-K α radiation) due to fluorescence radiation from the titanium atoms. As mentioned above the coatings with well defined crystallinity gave the fluorescence effect. However, the powder diffraction patterns obtained from the amorphous or low crystallinity coatings were clear with

negligible fluorescence effect although they were titanium bearing coatings. So in this case the fluorescence should not be ascribed to the titanium atoms but to the presence of iron atoms. The fluorescence effect was eliminated using an aluminium cover foil 0.02mm thick but the exposure time was increased from 6 hours to 16 hours in order to obtain the same intensity of the lines. As an alternative method of avoiding the fluorescence effect, iron filtered cobalt radiation was used for exposures of 6, 12 and 16 hours. The result was that fluorescence was satisfactorily eliminated but the lines obtained were faint and those with intensities lower than 50% were missing.

By examining the nature of the Debye-Scherrer films obtained it can be said that the coatings are very fine grained because the film lines are not sharp but always they appeared to be broadened. According to Cullity⁽⁷³⁾ the first signs of line broadening, due to small crystal size, begin to be detectable at about 10^{-5} cm (1000\AA). A size range between 10^{-5} and 10^{-3} (or 10^{-4}) cm, gives an X-ray diffraction which is quite insensitive to variation in grain size, with a continuous sharp ring pattern. It can be seen also that the coatings are homogeneous and there is not any kind of texture e.g. preferred orientation.

As Ranguram and Bunshah⁽³⁴⁾ report, vapour deposited films are well known to have varying amounts of preferred orientations. Investigating this fact in the case of titanium carbide coatings deposited by activated reactive evaporation process they reached the conclusion that considerable amounts of preferred orientation in $\{220\}$ plane exists at temperature below 830°C . As the temperature is

increased the texture transforms to a random texture. In the case of coatings deposited by chemical ion plating, although the substrate temperature, as explained in Chapter 5.1, was in the range of 419°C and 630°C , well below 830°C , no kind of preferred orientation was observed. This may be ascribed to the deposition mechanism of the coating which is continuously exposed to the high energy ion bombardment, thus preventing development of any preferred orientation.

(50)
Bunshah, based on the information of Bland et al, cites that in the case of sputtering, the texture changes are more complex than in the case of activated reactive evaporation, and vary primarily with the substrate bias. It is possible to consider that the same kind of mechanism is taking place in both sputtering and chemical ion plating since they use the same source of energy, that provided by the glow discharge.

In Table 15 are listed lattice constants for different titanium carbide coatings obtained under stable ion plating conditions, i.e. voltage 4kV, current 200mA and deposition time 3hrs. 10 minutes. The changing independent variable was the ratio of argon plus hydrogen and the carried titanium tetrachloride to acetylene gas in the reaction mixture. The intention of this investigation was to find the optimum ratio of gases which would give coatings of strict stoichiometric composition. This was because a number of investigators^{(18),(39),(66),(67),(68)} using different ion plating methods for preparation of different coatings, have made clear that the desired chemical composition in the coatings is a function of the particular ratio of the reactant gas volumes. This implies that when the gas reaction mixture is such that the prepared coating material is substoichiometric

the lattice parameter is smaller than the stoichiometric one. In the case of titanium carbide when it contains carbon between 11% and 20% by weight (stoichiometric ratio) the lattice parameter changes from 4.285\AA to 4.33\AA . This is widely reported in literature^{(27),(72),(74)}. Furthermore Rudy⁽⁷²⁾ reports that when titanium carbide contains free carbon, between 20 and 27% by weight, the lattice parameter does not change but it has a constant value equal to 4.33\AA . Also Schwarzkoph and Kieffer⁽⁷⁴⁾ report that preparation of overall composition $\text{TiC}_{1.5}$ and $\text{TiC}_{2.0}$ does not show variation of lattice constant and so they conclude that $\text{TiC}_{1.0}$ represents the upper phase limit.

Based on this information and also on the results obtained by electron probe microanalysis, Chapter 5.2.3, it can be seen that the coatings deposited by chemical ion plating, because they contain carbon which is well above the stoichiometric ratio (between 38 and 67.5% by weight carbon) should have a constant lattice parameter. On Table 15 the measured lattice constants of coatings prepared under different deposition conditions are given. Also on the same Table the carbon content calculated by electron probe microanalysis is also cited. By standard statistical treatment of the lattice constants and the content in carbon it was found that there is a low probability that these two variables are related since their coefficient of correlation is only 0.412. The mean value of the measured lattice constants is 4.347 ± 0.009 . So it is concluded that under the conditions used the coatings prepared have a constant lattice parameter since they always contain free carbon.

On the graph of Fig. 20 the measured lattice constants versus the weight content in carbon are given and the mean value line is drawn. On the same graph the curve corresponding to carbon content below 27% in weight, according to Rudy⁽⁷²⁾ is also given. From this graph it can be seen that the material produced in current work has a lattice constant 0.017\AA ⁰ bigger than that given by Rudy. Taking into account the results obtained by electron probe microanalysis, chlorine was shown to be present in all samples prepared under compositions of reaction mixture used and so it could be argued that the swelling of the unit cell was due to the presence of the chlorine atoms, which may occupy some of the octahedral voids in place of carbon atoms. The much higher radius of chlorine atoms (0.99\AA)⁰ than that of carbon atoms (0.77\AA)⁰ may offer a possible explanation of the enlargement of the lattice constant.

Another possible explanation is that the titanium carbide coatings because were deposited at low temperatures below 1000°C where no annealing of titanium carbide can take place then they are under stress. It is known that such an effect creates both line broadening and shifting of the lines on the Debye-Scherrer films. To investigate this, two samples were annealed at 1400°C in a stream of $\text{N}_2 + 25\%\text{H}_2$ for 2 hours and then analysed using the diffractometer method. The result was that the peaks corresponding to titanium carbide were sharpened and higher in intensity but the lattice constant obtained was much smaller than that accepted for stoichiometric composition. From this experiment it can be inferred that though chlorine may contribute to the increase of the lattice parameter, stress in the coating is also significant.

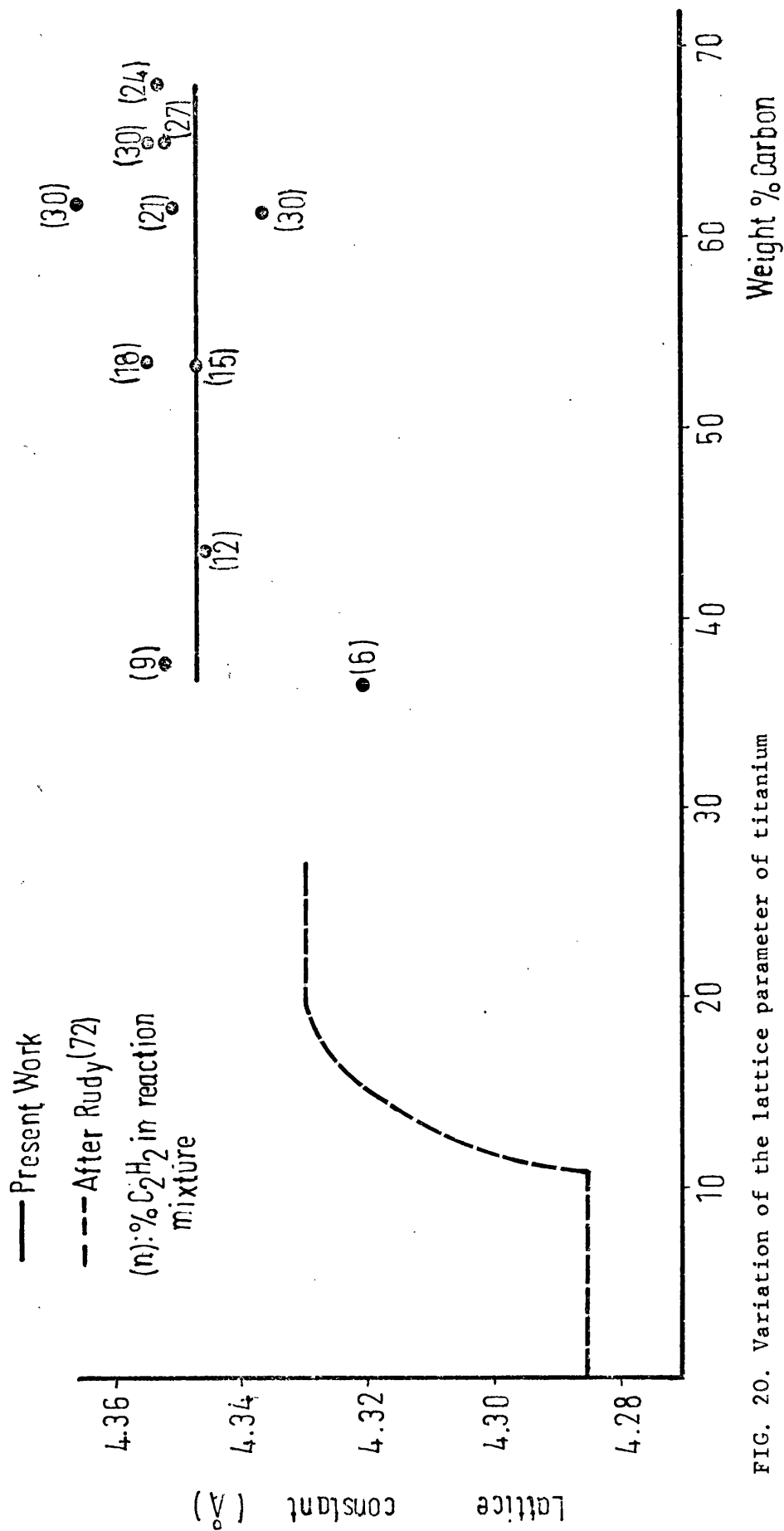


FIG. 20. Variation of the lattice parameter of titanium

carbide with the carbon content.

estimated by E.P.M.A.

It is interesting to note that on the Debye-Scherrer films there is no suggestion of free titanium, its oxides or graphitized carbon being present in the coating as the only lines are those from titanium carbide although according to the electron probe microanalysis results, there is an excess of carbon. Finally, as can be seen from Table 15, the voltage applied to the cathode-specimen does not appear to affect the lattice parameter significantly. It also appears that a reduced current density does not affect the lattice constant.

5.2.2. Microstructure

As mentioned in Chapter 5.1, the titanium carbide coatings had to be left for about 24 hours before any preparation was undertaken for metallographic sectioning. After that time interval, due to an aging effect, it was possible to start cutting the samples for microscopic examination, without any problem of coating failure like delamination, during the whole procedure of preparation for microscopy. The metallographic investigation had the intention of revealing the structure of the coating if any, the existence of defects like porosity and finally to estimate the thickness of the coating.

The preparation of sections which are smooth at the edges is a very important condition for any success in metallographic inspection. The preparation of such sections was difficult due to the high hardness, brittleness and the low thickness of the coatings. In order to obtain the cross-section on which the coating was well preserved in situ without any detachment from the substrate extra care was needed. First of all after cutting the substrate, with a hacksaw, the sample was mounted by hot pressing in bakelite. Then it was lapped on a 600# silicon carbide paper and finally it was polished by means of 1µm diamond paste. The lapping and polishing was done in such a way that the coating was always exposed to the polishing wheel movement so that it was continuously under compression. Thus, having the backing of the substrate, material was not detached, as could happen in the case when the coating was under tension.

Although, after the polishing preparation, the coating could be seen easily under the microscope, due to its different colour, however, etching in 2% Nital was carried out in order to observe the interfacial region, and also to determine exactly the substrate to coating boundary

for film thickness measurement.

By doing this two different effects were revealed. First, a change in composition of the upper layers of the steel substrate and second the existence of an interlayer between coating and substrate. The steel appeared to be decarburized and the thickness of the decarburized zone was approximately 85 to 90 μ m while the thickness of the interlayer was approximately 1 μ m. Both of these can be seen on Fig.21. In order to check the assumption of decarburization, microhardness measurements were taken across this zone and the unchanged mild steel region. The results of this measurements show that while the unchanged mild steel region had a microhardness value of 270 kg mm⁻² (using 20 g load), the microhardness of decarburized region was 210 kg mm⁻², which means that, this region transformed to ferrite since the carbon of the pearlite has been removed.

Such a decarburization effect is known in the cases of chemical vapour deposition method when titanium carbide is deposited on low carbon steel substrates. Ruppert⁽⁴⁹⁾ reports that, due to deposition of titanium carbide the activity of carbon in the reaction gas may become smaller than the activity of carbon in the base. Then carbon of the upper layers of the base diffuses through the titanium carbide coating into the reaction gas if the temperature is high enough to permit this diffusion. Similar reactions may also happen if the carbon of the base reacts much more quickly than the hydrocarbons of the reaction gas with the deposited titanium. In chemical vapour deposition of titanium carbide onto high carbon steels the decarburization of the upper layers of the base is often not

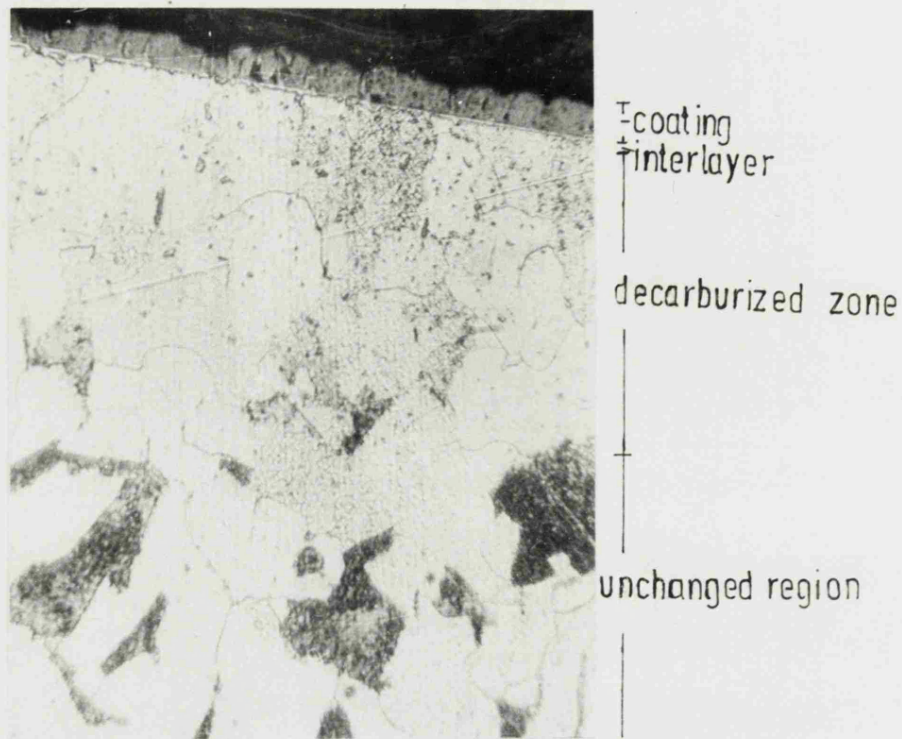


Fig. 21.

17 μ m



Fig. 22.

62 μ m

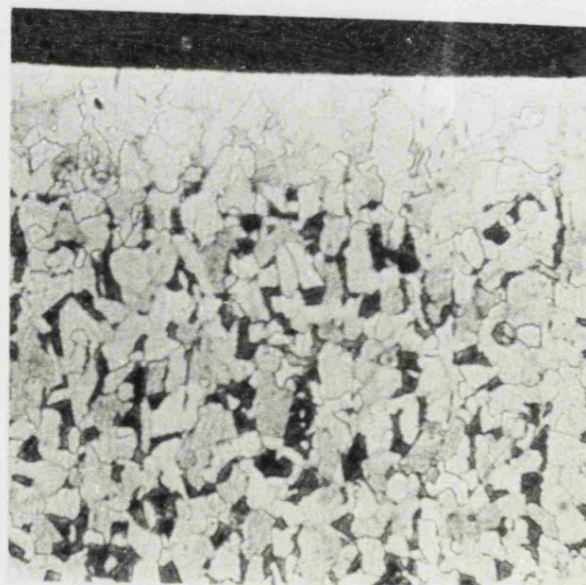


Fig. 23.

62 μ m

Fig. 21 Cross-section of coated mild steel substrate, etched in 2% Nital

Fig. 22 Cross-section of coated mild steel substrate, etched in 2% Nital

Fig. 23 Cross-section of uncoated mild steel substrate, sputter-cleaned in argon glow discharge under the conditions voltage 4kV, current 200mA, time 35 min. Etched in 2% Nital

observed, because the decarburization does not yet produce ferritic interlayers; but the content of cementite in the upper layers of the steel is reduced. However, this mechanism is unlikely to happen in the case of chemical ion plating. It can be seen that coated samples with titanium carbide which have been exposed to 35 min. of sputter cleaning and 3 hours and 10 min. of deposition compared to uncoated samples exposed only to sputter cleaning for 35 min. under the same conditions of voltage (4 kV), current (200 mA) and pressure (40×10^{-3} Torr) show the same depth of decarburization. This means that the decarburization takes place during the sputter cleaning period and ceases after the first layer of titanium carbide formation. This is illustrated on Fig.22 and 23. On the top of the substrate of Fig.22. the titanium carbide layer can be seen. However, it is unlikely that the normal decarburization mechanism which can take place in presence of carbon dioxide or oxygen at high temperatures is occurring, since under vacuum the oxygen activity is low. So the cause of carbon loss from the substrate is not chemical reaction with oxygen, but probably sputtering due to ion bombardment. This supposition seems to be compatible with the reported sputtering rates of various materials. According to Holland⁽⁷⁾, who cites the sputtering rates of different metals into a hydrogen discharge, the rate corresponding to carbon is approximately 20 times higher than that of iron. Since the disintegration rate in sputtering increases with atomic weight of the gas, i.e. it is greatest in argon and least in hydrogen, it can be understood why the carbon of the surface of the substrate is sputtered more easily than the iron.

The mechanism which extracts the carbon atoms from depths of

85-90 μm and carries them up to the surface seems to be that of thermal diffusion. Taking into account Fick laws of diffusion it can be calculated that a mild steel substrate exposed to decarburizing conditions can be decarburized up to a depth of 90 μm in 20 min. if the temperature is 580°C⁽⁷⁵⁾. Since the cathode substrate reaches 419°C (melting point of zinc) after 10 min. of continuous bombardment of its surface by argon ions (Chapter 5.1), it can be supposed that in 15 min. the temperature will rise to the necessary range of temperatures where decarburization is completed. (Table 16 gives the times in minutes required to decarburize depths of 90 μ and 100 μm at different temperatures, and also the corresponding calculated values of diffusion coefficient D for carbon⁽⁷¹⁾). Then even if it is accepted that the temperature does not rise any further in 20 min. remaining it is possible to decarburize the substrate layer in a depth of 90 μm . So in the 35 min. of sputter cleaning there is sufficient time for both heating of the substrate and diffusion of carbon.

As would be expected, lower discharge power, i.e. voltage 4 kV at current 50 mA under the same time of 35 min. sputter cleaning would produce a thinner decarburized zone. Relevant experiments showed that the decarburized zone was 50 μm .

Examining the micrographs of the cross-sections from the martensitic substrates it can be seen that a pure ferritic layer is not formed but as depicted from Fig.24 the content of cementite in the upper layers of the steel decreased.

Concerning the interlayer material which exists between the substrate and the coating Ruppert⁽⁴⁹⁾ reports, this consists of materials

TABLE 16. Decarburization details of mild steel at different temperatures.

Temperature °C	Diffusion coefficient D cm ² sec ⁻¹	Time required in min. to decarburize a zone of	
		90 μm	100 μm
500	1.14 x 10 ⁻⁸	118.2	145.9
520	1.84 x 10 ⁻⁸	73.0	90.0
540	2.91 x 10 ⁻⁸	46.2	57.1
560	4.51 x 10 ⁻⁸	29.9	36.9
580	6.83 x 10 ⁻⁸	19.8	24.4
600	1.01 x 10 ⁻⁷	13.3	16.4
620	1.48 x 10 ⁻⁷	9.1	11.2

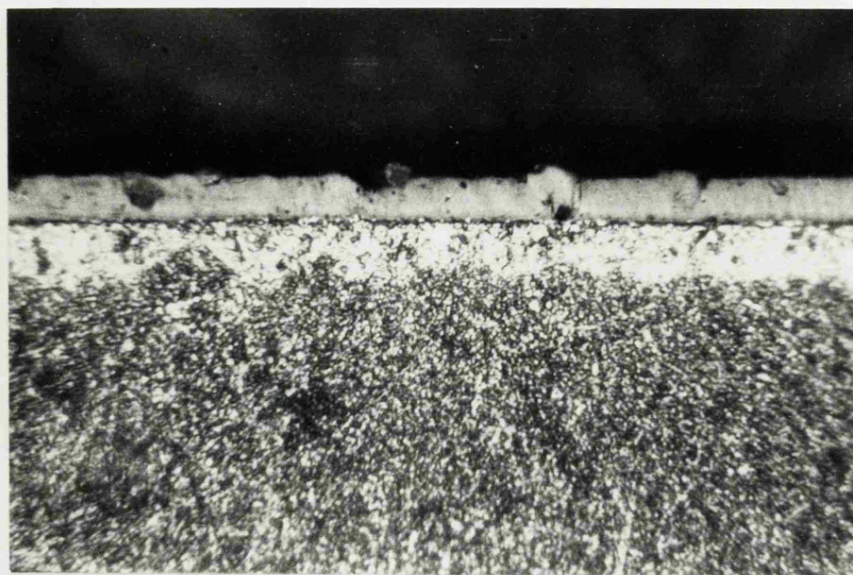
which are stable or almost insoluble in the substrate and coating material, or which diffuse very slowly at reaction temperature. The thickness of the interlayer is constant all over the surface of the specimen-cathode and seems not to depend on the gas reactants composition. Another fact which is worth noticing is that it fills up the grain boundaries fissures which had been created by the ion bombardment etching. This can be seen in Fig.25. So all the active surface exposed to the reactants participates in the interlayer formation.

In the case of the martenitic steel substrates the interlayer either does not exist or is locally isolated.

The practical effect of the presence of the interlayer material is deleterious because leads to the spalling of the coating during the cooling period and some time during the first 24 hours after removal from the chamber. If this interlayer is an intermetallic compound then due to its brittleness and due to the inherent stresses produced during the coating formation as a result of the differences in lattice parameters with the substrate material and also due to thermal stresses on cooling, spalling is probable.

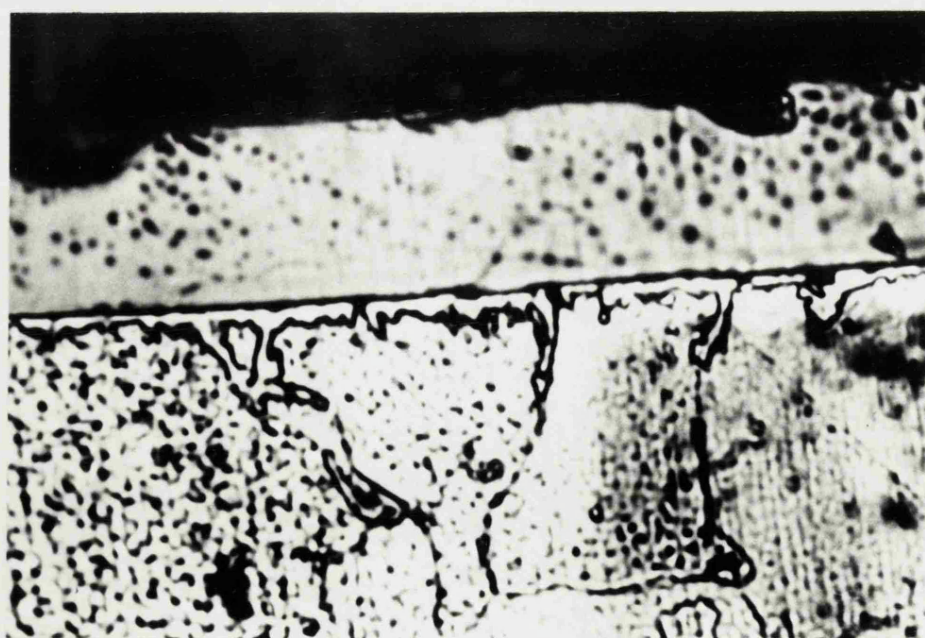
While specimens of titanium carbide coating onto mild steel substrates and from gas composition between 18% and 30% C_2H_2 , showed always areas, mainly around the central region of the upper surface, which had already spalled before their removal from the chamber, the specimens produced from the carburized steel substrates which did not show any sign of spalling.

During trials of chemical etchants for detecting the grain size



17 μm

Fig. 24 Cross-section of coated carburized steel substrate, etched in 2% Nital

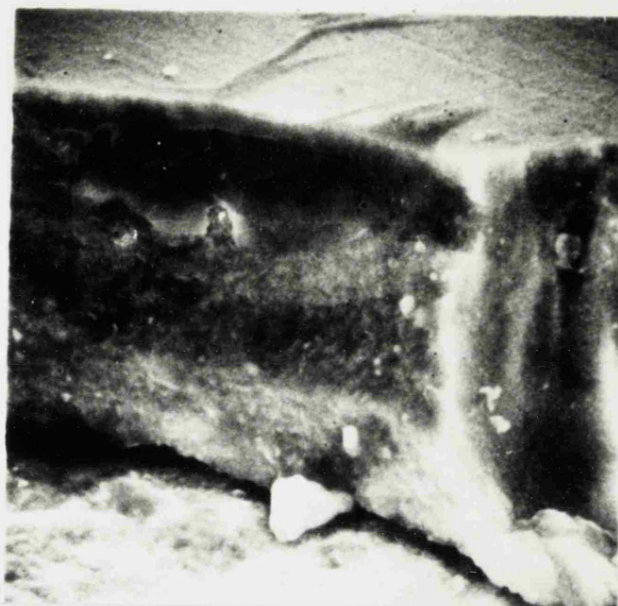


4.65 μm

Fig. 25 Cross-section of coated mild steel substrate, etched in 2% Nital

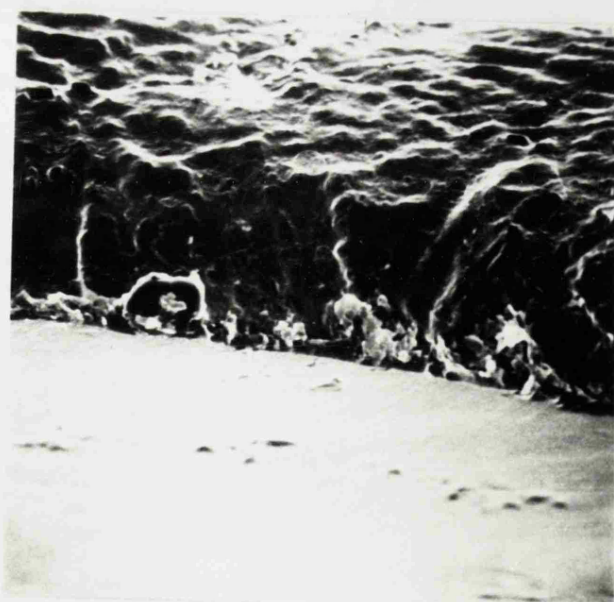
and the structure of the coatings, it was observed that some of the reagents tried, such as aqua regia or 5% hydrofluoric acid, attacked the material of the interfacial region and the coating was stripped off as small fragments. This is because titanium carbide is electrochemically more noble than iron base materials⁽⁴⁹⁾. Hence, the interlayer of the intermetallic can be so deeply attacked by the etchant that it can no longer be detected. Fig.26 shows a section of the coating after attack by 5% HF. At the base of the picture can be seen a crevice which has been created by the dissolution of the intermetallic compound, while it can be seen the substrate, the coating and its surface remained unattacked.

To find out the grain size of the obtained coatings, the surface of the coated sample was polished by means of 1µm diamond paste. The polishing was continued up to the point that all the nodules and asperities were just removed. An investigation was made to find if the microstructure of the coatings could be revealed by etching. The etchants used were: the Murakami reagent (10g KOH, 10 g $K_3Fe(CN)_6$ in 100 cm³ of H₂O) as it is suggested by Toth⁽²⁵⁾, Smithells⁽⁷⁶⁾ e.t.c., aqua regia, nitric acid of different concentrations (2% up to 20% by volume in water) hot concentrated nitric acid as was used by Takahashi et al⁽⁷⁷⁾ for etching titanium carbide coatings deposited by chemical vapour deposition, hydrofluoric acid (2% up to 5% by volume in water). The etching times varied from seconds up to 10 min. The only effect seen and then only in the cases of 5% hydrofluoric acid and aqua regia, as mentioned above, was the attack on the interfacial material. Otherwise no etching effect on the coating was observed even at magnifications up to X 10.000. This means that the grain size is smaller than 1000 Å, a size which would be easily detected under such a magnification.



1 μ m

Fig. 26 Cross-section of the coating
after attack by 5% HF



5.2 μ m

Fig. 27 Cross-section of the coating
after attack by aqua-regia

Examining the microstructure of coatings in cross-section using optical and stereoscan electron microscopy showed that the coatings are free of gross defects such as porosity and pinholes (Fig.27) and consists of very fine grains the size of which is smaller than 1000 \AA (Fig.26). These figures show clearly the dense nature of the coatings and also do not indicate any particular mode of nucleation or any mode of coatings build up.

Pores which are formed preferentially at sharp edges, scratches and holes in other methods as in vacuum evaporation⁽²⁾ were not detected even at high magnification ($\times 10,000$). The dense, void free nature of the deposits can be ascribed to the mobility of the coating particles. The mobility comes as a result of two complementary factors:

- a) the momentum of the bombarding particles and
- b) the temperature of the surface layer.

Carson⁽⁷⁸⁾ who had deposited by rf-diode sputtering titanium oxycarbides reports that when porosity was visible, increasing the amount of negative bias to the substrate caused a reduction in this porosity. Characteristically, he says that coatings deposited without any bias showed porosity and at -60 V no porosity was observed. He ascribes this to the increased mobility of the surface atoms caused due to the negative bias. This increased mobility comes from energetic particles which bombard the surface. Transfer of the momentum of these bombarding particles to the coating material tends to fill any coating voids. Thus a negative potential of -4 kV , which is used in the chemical ion plating, ought to give even more dense coatings.

Concerning the influence of substrate temperature, Bunshah⁽³⁸⁾ reports that the higher temperature of the substrate surface, and also the greater the kinetic energy of the incoming atom, the denser will be the resultant structure. The temperatures which he is speaking about are of the range of 500 to 650°C i.e. the temperatures created in the chemical ion plating, of titanium carbide.

Concerning the extra fine size of the deposited coatings this can be ascribed to the nucleation of new grains by the localized temperature spikes at the vapour-solid interface due to ion bombardment. Bunshah and Juntz⁽⁷⁹⁾ deposited beryllium on a biased substrate to -5 kV at a temperature of 570°C, and found that the columnar grain size was markedly refined by the ion bombardment as compared to the grain size produced without biasing the substrate at the same deposition temperature. It may be postulated that the ion bombardment causes a localized increase in temperature at the surface where deposition is occurring thus causing a higher nucleation rate and a finer grain size.

5.2.3. Examination by Electron Probe Microanalysis

Electron probe microanalysis is a flexible technique for elementary analysis of solid materials which is based upon the excitation of X-ray from a small portion of the sample by a beam of electrons, the emitted X-rays being analysed and counted by an X-ray spectrometer and detector. An electron beam produced by a conventional hot filament source is focused onto the specimen causing some of the atoms to be ionised via a mechanism involving the loss of an inner electron. The resultant transition of an outer electron involves the emission of an X-ray photon which is characteristic of the excited atom, and thus the emitted X-ray spectrum is characteristic of the elements present within the excited portion of the sample.

Qualitative analysis of a sample is performed by obtaining the sample count rate of the element of interest.

Quantitative analysis is also performed by obtaining the ratio of the sample count rate to the count rate of a standard, which is a well characterized compound containing the element of interest. However, various effects combine to make quantitative analysis less straightforward, notably absorption by surrounding atoms, fluorescence, electron back-scatter, secondary electron emission and the efficiency of the process of X-ray emission.

The principal advantages of electron probe microanalysis are:

- a) the technique can be applied to all elements of atomic number higher than 3 and
- b) analysis of small areas of interest may be performed with relative ease compared to other techniques, typical excitation volumes being approximately $2\mu\text{m}$ cube.

The limiting sensitivity of the technique is theoretically about $10\mu\text{g.g}^{-1}$ of sample. This figure, however, can only be achieved using the maximum possible care and specially modified apparatus of high sensitivity; a more realistic limiting sensitivity for normal operation is a factor of a hundred lower i.e. about 1mg.g^{-1} (80)

To a first approximation, the concentration of an element is linearly dependent upon the ratio of the X-ray count rate compared to that from the standard. Taking this assumption into account it can be expected that by changing the composition of the sample, the elements present will provide X-ray count rates which are proportional to their weight concentrations in the sample.

Based on this assumption the samples which were produced under the same conditions of glow discharge (voltage 4 kV and current 200 mA) but under different composition of gas reactants (6% to 30% in C_2H_2 and in intervals of 3%) were analysed by this method. The analysis was concerned for the elements; titanium, carbon, chlorine and oxygen.

The instrument used in this work was a JEOL JXA 50A analyser, which is designed with a 35° take off angle for X-ray emission. From the specimens prepared under the above mentioned conditions of ion plating, a sample (1 cm x 1 cm) was cut which fitted in the specimen holder. The coated surface under examination was checked for being in the plane of the top of the specimen holder by the optical microscope of the instrument having a narrow depth of focus. After setting up the electron probe microanalyser the electron beam was checked for focus and a specimen current of 60 nA of an accelerating voltage of 20 kV was used. This current was sufficient to obtain reasonable X-ray count rates of the order of 10^4 cps for titanium and 10^3 cps for carbon and chlorine.

The beam area was estimated to be approximately $0.80\mu\text{m}^2$. The X-ray detector was focused on the $K\alpha$, X-ray emission of the elements under investigation using a lithium fluoride crystal to resolve the X-ray emission of titanium, lead stearate crystal to resolve carbon and oxygen and a P.E.T. crystal to resolve chlorine. The X-ray counts were measured using a flow proportional counter. The measured count rates were those corresponding to the peak intensity for each of the analysed elements. The background count rate was also measured for each of the above elements (typically 20 cps) and the subsequent count rates were corrected subtracting the value for the background so obtained. The specimen was then scanned at a rate of $200\mu\text{m min}^{-1}$ along the coating surface. For ensuring homogeneity of the composition of the specimens scanning on two different directions took place i.e. along the radius of the original sample and on the perpendicular to this direction. The length of the scanned distance was $600\mu\text{m}$. The obtained count rates along the scanned distance were constant for the elements titanium and chlorine but varied in the case of carbon. Typical values of count rates for titanium were 2,000 to 4,500 with standard deviations 60 to 110. Typical corresponding values for carbon were 390 - 1000 with standard deviations 45 - 290. These big changes in carbon count rates were the result of topographical effect of the nodules which are protruding above the matrix of the coatings as explained in Chapter 6.1. After polishing the surface and removal of the nodules the variation in the count rate was ± 20 cps.

The qualitative analysis showed that the elements present in the analysed coatings were, titanium, carbon and chlorine. It is worth noticing the absence of oxygen in the coatings obtained. The level

of oxygen count rates in the whole series of the analysed specimens never was above the background level. This is significant because preparation of titanium carbide free of oxygen by methods like sintering is difficult and the oxygen impurities give titanium monoxide. Titanium carbide forms solid solutions with the isomorphous titanium monoxide⁽⁷⁴⁾ resulting in a lower lattice parameter of the formed carbide⁽²⁷⁾. As was noticed by X-ray powder diffraction fluorescence due to iron occurred. (Chapter 5.2.1.) However, detectable quantities of iron were absent when checked by electron probe microanalysis.

To find out if the composition of the coating remains the same in depth, electron probe microanalysis carried out on cross-sections of specimens. The results showed that the count rates obtained for the elements were the same along the whole depth of the coating and agreed with the corresponding measurements obtained from the surface analysis.

From this it is inferred that the coating material is deposited in the same mode during the whole deposition period. Such an analysis was feasible because the coating thickness (between 6 μ m and 12 μ m) was greater than the volume of material analysed.

An additional reason for performing electron probe microanalysis along the cross-sections was to find if diffusion, of depositing atoms into substrate materials has occurred. However, it was not possible to detect diffusion over any significant distance, (i.e. greater than 1 μ m). Even the interlayer which was detected by optical microscopy, as mentioned in Chapter 5.2.2. and it is shown on Fig.25, could not be detected by this method, because the thickness of the interlayer was only 1 μ m and as mentioned previously the volume analysed

using electron probe microanalysis is greater than this. One can speculate about the likely composition of this layer. As has been mentioned in Chapter 5.2.2 the surface of the substrate after the sputter cleaning period becomes ferritic and thus the major element present is iron. The element coming to the substrate from the gas phase are mainly titanium and carbon. Thus the compound could be either a binary compound between titanium and iron or a ternary one between titanium, iron and carbon. However, no ternary titanium-iron-carbides are reported in the ASTM index so this type of compound seems improbable. The remaining possibility is that of binary compounds. According to Hansen⁽⁸¹⁾ and also to ASTM filing system there exist the TiFe_2 and TiFe as the only binary compounds of titanium and iron. So one of these or either can constitute the interlayer material.

To analyse quantitatively by this method the prepared coatings it would have been preferable to use titanium carbide crystal of known composition. However, since it proved to be difficult to acquire such a crystal which would be large enough for reliable analysis, crystals of pure titanium and potassium chloride of known composition were used.

The spectrometer was set on the X-ray peak of interest (chlorine or titanium) and the X-ray intensity from both specimen and standard was measured. The amount of chlorine in the specimens was known to be small and hence no corrections for atomic number effects or absorption was employed. The chlorine concentration was determined using

$$C_{\text{spec}} = C_{\text{KCl}} \frac{I_{\text{spec}}}{I_{\text{KCl}}}$$

where C_{spec} and C_{KCl} are the weight concentrations of chlorine in the specimen and potassium chloride respectively and I_{spec} and I_{KCl} are the corresponding X-ray intensities from chlorine. The corrected titanium concentration is determined by assuming that the specimen contains only titanium and carbon. This is reasonable since absorption of titanium $K\alpha$ radiation in both chlorine and carbon is similar and chlorine levels are low. The weight concentration of titanium in the specimen is then calculated in the conventional manner using the correction for atomic number, absorption, and fluorescence (ZAF) which has been developed by Love, et al⁽⁸²⁾. Finally, carbon concentrations are found by subtracting the known titanium and chlorine concentrations from 100%. The results obtained of the measured weight % of titanium and chlorine are given on Table 17. On the same table the estimated weight % of carbon is also given.

Finally, on the same table three results for carbon concentrations obtained by chemical analysis (combustion and gravimetric determination of the produced CO_2)⁽²⁵⁾ are also shown. The amount of samples analysed was small (below 50 mg) and as such may incorporate a substantial uncertainty. However, it can be seen that the analytical results obtained have a difference with the corresponding estimated by EPMA of about 10 - 15%. The results obtained by EPMA are illustrated on graph of Fig.28.

Comparing the carbon content of the samples obtained by chemical ion plating with the stoichiometric composition (20% by weight in carbon) it can be seen that the obtained coatings contain excessive amount of carbon. So the coatings deposited must be a composition of titanium carbide plus free carbon. However, this free carbon must be very finely grained (below 1000 Å) as it can not be resolved even at high magnifications such as X 10,000. It must also be amorphous

TABLE 17. Analytical results of titanium carbide coatings deposited under different compositions of reaction mixture at voltage 4 kV and current 200 mA.

C ₂ H ₂ % by volume in reaction mixture	Weight %			
	by E.P.M.A.			by chemical analysis
	Measured		Estimated	Measured
	Ti	Cl	C	C
6	58.67	3.63	37.70	
9	58.67	3.47	37.86	
12	52.45	4.15	43.40	
15	43.05	4.00	52.95	
18	43.61	3.52	52.87	
21	35.26	3.34	61.40	
24	29.42	3.18	67.40	59.1
27	30.01	3.17	64.82	
30	31.36	3.53	65.11	68.45
30	35.26	3.44	61.30	56.33

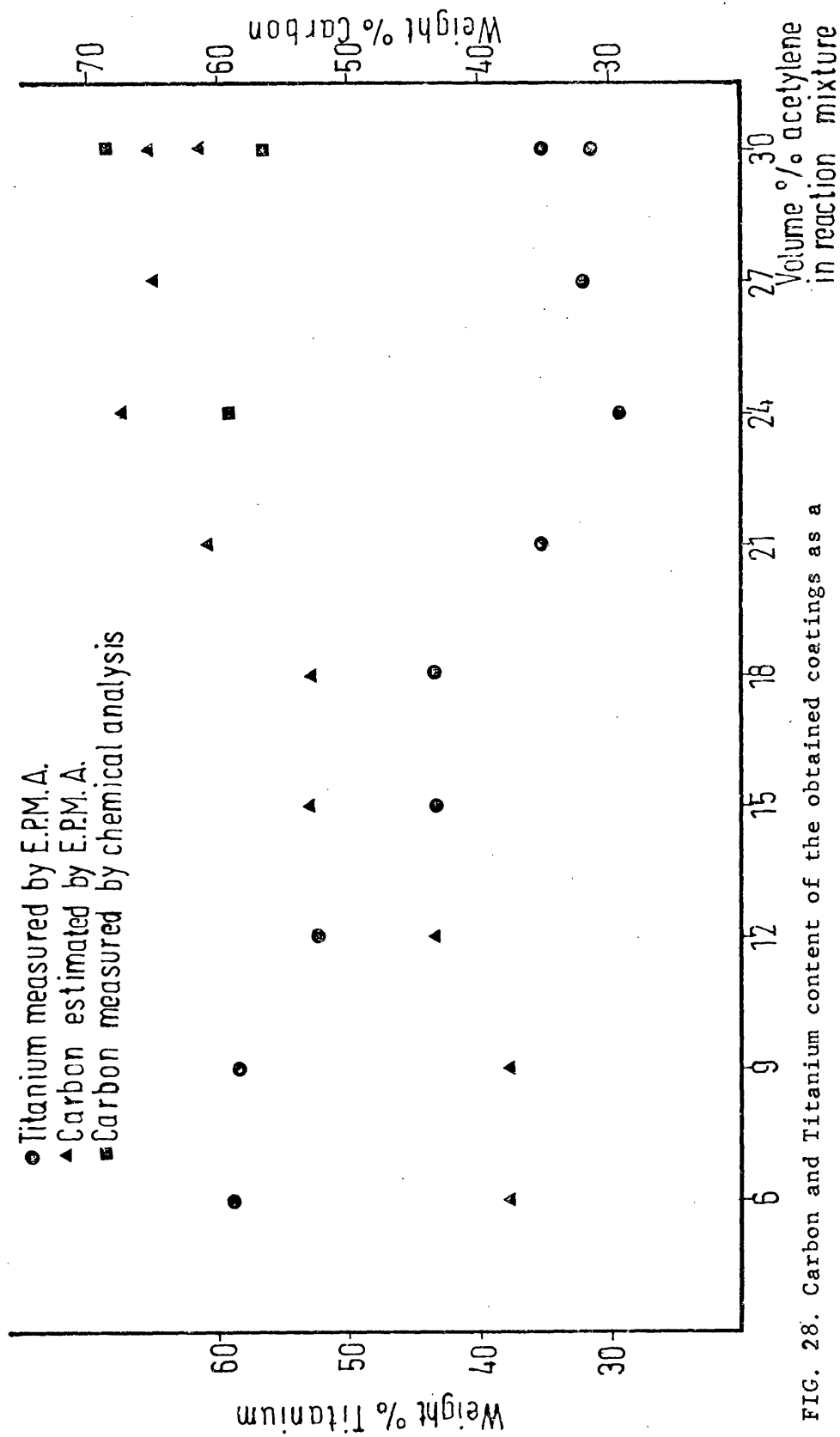


FIG. 28. Carbon and Titanium content of the obtained coatings as a function of the content of acetylene in the reaction mixture.

non-graphitic because it can not be detected by X-ray diffraction techniques.

CHAPTER 6

MEASUREMENTS OF PROPERTIES

6.1 Topography of the coatings surface

The as-deposited surface finish of a hard coating is very important because smooth surfaces are required in most mechanical applications. The amount of work required to lap or grind a coating surface to a particular finish may significantly affect the economics of using a coating⁽⁸³⁾.

Examining microscopically the surfaces of the as-deposited coatings it can be seen that they are not smooth, but on the contrary, they have a dull appearance. A representative picture is given in Fig.29. It can be seen that on the flat matrix of the titanium carbide coating numerous semispherical nodules of varying sizes from 4 to 12 μm are present. Representative large nodules are given in Fig.30 and Fig.31 and as can be seen they project above the surface. Between the nodules and the rest of the matrix there is not a smooth transition but apparently some evidence of undercutting (Fig.30) and (Fig.31) giving the impression that these agglomerates are formed in the vapour phase and impinge on the already formed matrix with a very high velocity. But as already has been explained in Chapter 3.1 agglomerates which may be formed in the vapour phase due to the negative charge which they obtain, do not move the cathode but to the anodic parts of the chamber. So this assumption seems unlikely.

Furthermore, when cross-sections of these nodules were examined (Fig.32) it appears to form a continuous extension of the matrix than appearing as an attached particle. The slight cracking appearing at

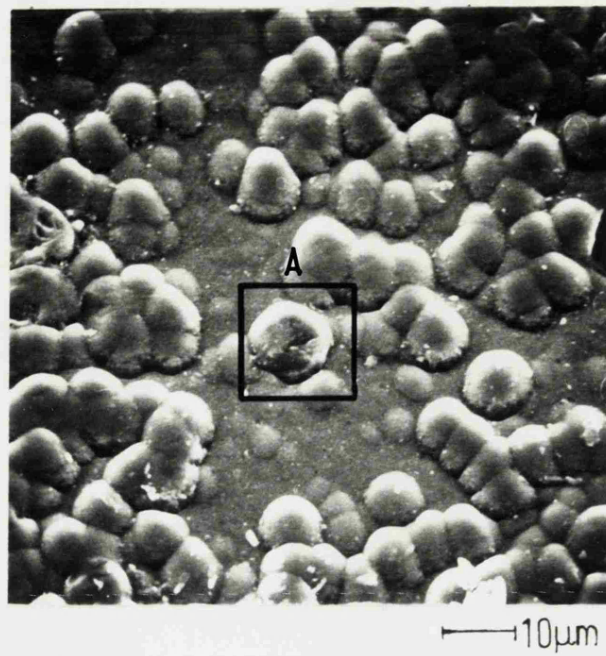
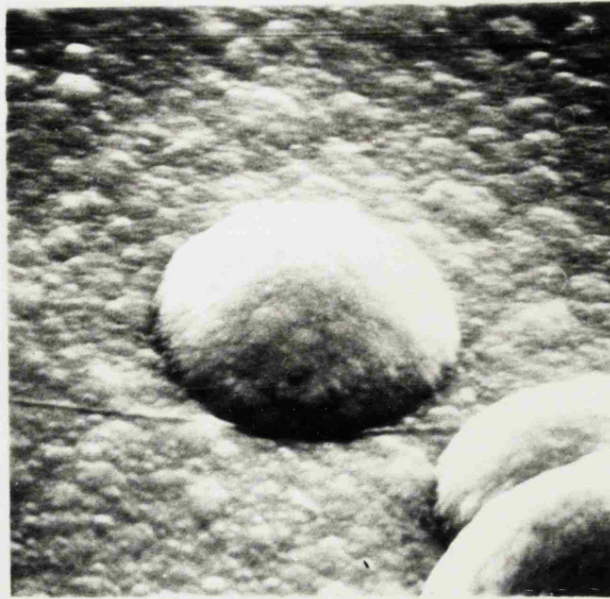


Fig. 29 SEM photograph representative of the surface of the titanium carbide coatings obtained



Fig. 30 SEM photograph of the module in square A of Fig. 29



1.9 μm

Fig. 31 SEM picture of a representative large module on a titanium carbide coating



1.7 μm

Fig. 32 SEM picture of a cross-section of a coating which shows the cross-section of a module

the left hand side of the picture almost certainly arises from the unidirectional polishing necessary, due to the brittle nature of the film material. Similar cracking was observed in all seven sections prepared in identical geometrical positions.

The phenomenon of nodules formation is reported in cases of chemical vapour deposition coatings. Archer⁽⁸³⁾ reports that preparing tungsten carbide (W_2C) coatings by CVD on nickel-plated steel large nodules (approximately $100\mu m$) were obtained and suggested two major reason for their creation. First the smoothness of the steel substrate and second the high concentration of reactant gases (tungsten hexafluoride and benzene).

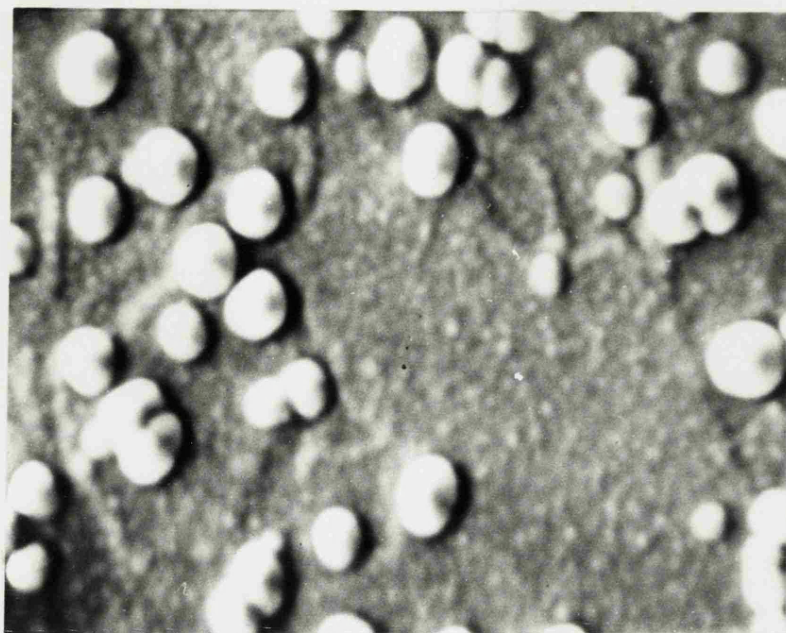
Spitz and Chevallier⁽⁴⁴⁾ report that preparing tantalum coatings, they observed the presence of nodules of tantalum both in the case of chemical vapour deposition and also of ion plating, when the substrates were fixed. They claim that the nodules, which some times attain diameters of $20\mu m$, are caused by self-shadowing effect and may be eliminated by displacing the substrate in the vapour flow. Enomoto and Matsubard⁽⁸⁴⁾ depositing by ion-plating, copper onto tungsten substrate they found that the surface of the coating was pebble-like or dome shaped.

Raghuram and Bunshah⁽³⁴⁾ depositing titanium carbide on tantalum substrates by activated reactive evaporation, have found that at low substrate temperatures, below $520^{\circ}C$, the surface had a domed structure and that at temperatures above $610^{\circ}C$, this structure disappeared. For explaining this phenomenon they consider that the type of surface structure, texture and grain size are very intimately related to the

purity of the deposit and the surface condition of the substrate, the bonding between the deposited material and the substrate material, residual stresses, possible solid-solid transformation in the deposits and the rate of deposition, and they suggest that further experimentation is needed to sort out the variables controlling structure. It seems likely that the same controlling variables determine the formation of nodules and in the case of titanium carbide coatings deposited by chemical ion plating.

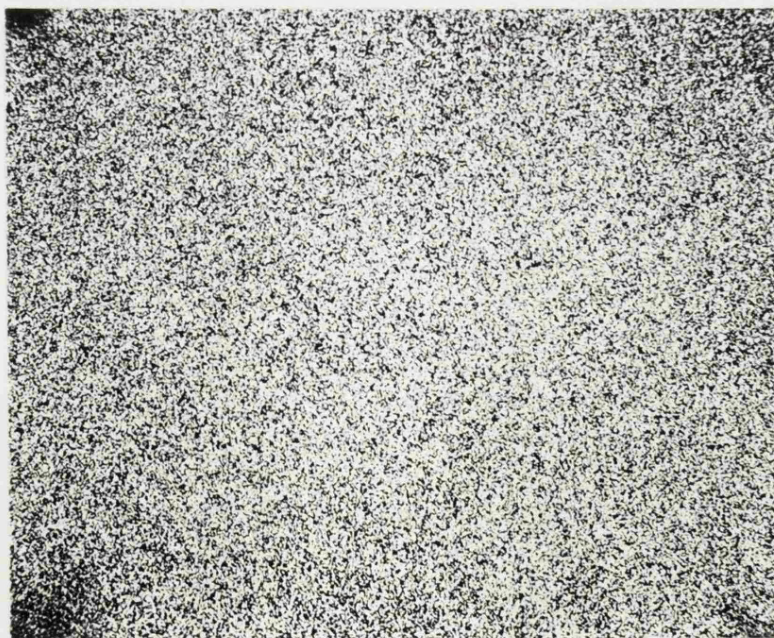
When, at the first stages of the investigation, the presence of the nodules was noticed an examination by the electron probe microanalyser was carried out, to find out their nature. The analysis conditions were the same as those described earlier (Chapter 5.2.3.) The X-ray pictures of the peak intensities for titanium-K α , chlorine-K α and carbon-K α obtained gave no indication of any change of concentration of these elements at the places where the nodules were, as shown on the corresponding picture (Fig.33) of the same area. The obtained X-ray pictures can be seen on Fig.34, Fig.35 and Fig.36. Only the carbon concentration appears to change in the regions of the nodules but this can be ascribed to surface topography because carbon-K α X-rays are strongly absorbed by the matrix. When the surface was polished and the nodules were just removed the carbon X-ray emission became uniform (Chapter 5.2.3.). This would seem to eliminate the possibility that the nodules are second phase particles.

Another detail which should be mentioned is the behaviour of the nodules under wear resistance experiments. Experiments carried out for friction coefficient measurements under load of 13N and speed of the stainless steel counterface 2rpm, shown after one hour of running



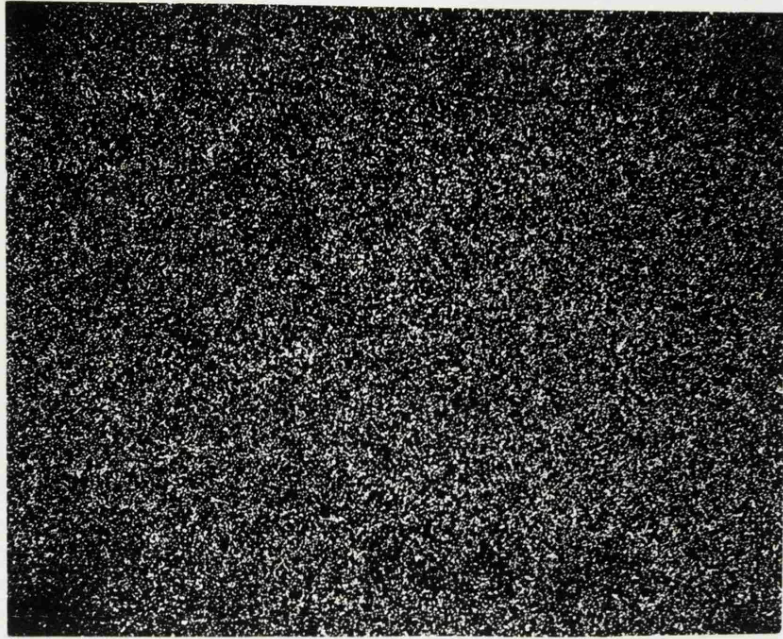
10 μ m

Fig. 33 Electron Picture of surface area
of titanium carbide coating



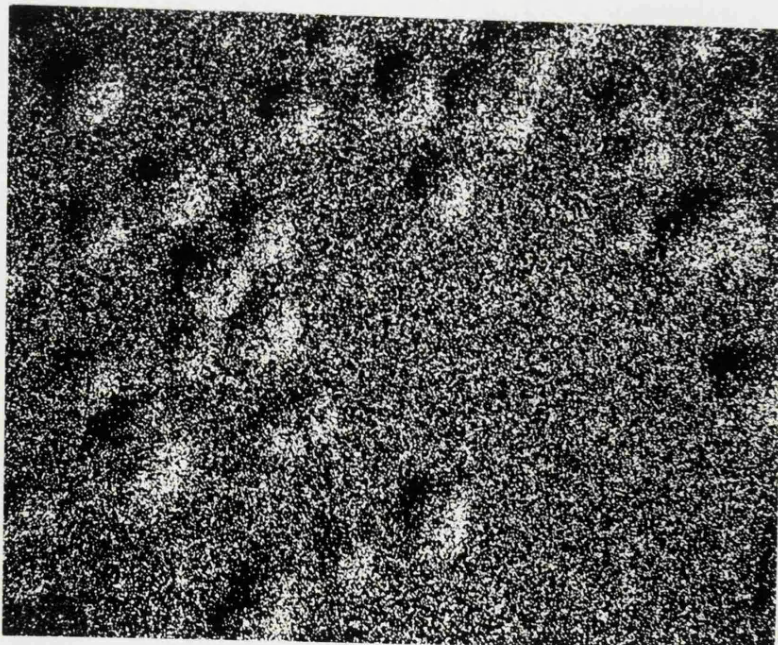
10 μ m

Fig. 34 X-ray picture showing the
distribution of titanium of the area of
Fig. 33



10 μ m

Fig. 35 X-ray picture showing the distribution of chlorine of the same area of Fig. 33



10 μ m

Fig. 36 X-ray picture showing the distribution of carbon of the area of Fig. 33

that the nodules which protruded high above the others of smaller size were partially worn while these of smaller size and the main matrix surface were intact. The wear of these large nodules take place in thin layers parallel to the counterface surface without any detachment of fragments from the rest of their mass, or the most important any detachment of the whole nodule.

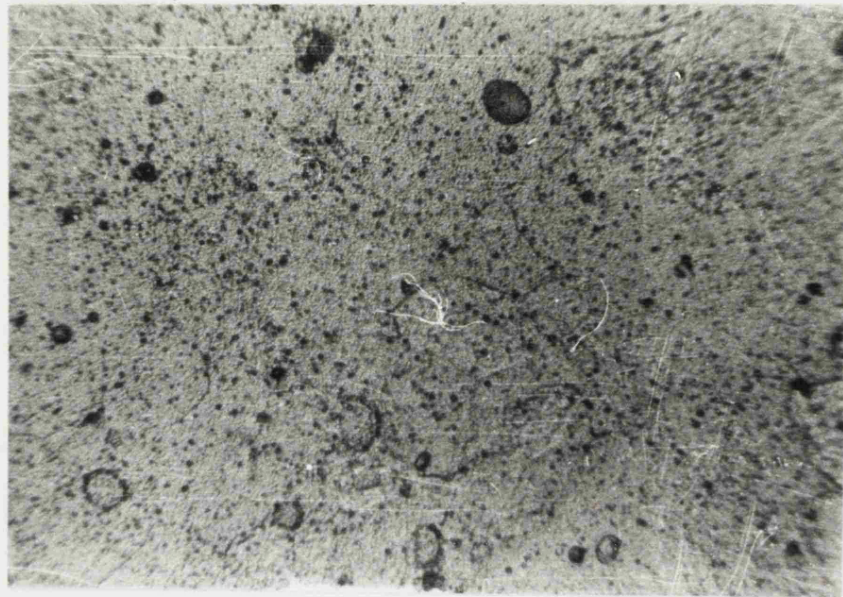
Furthermore, the hardness of the titanium carbide coatings is such that it can be lapped by silicon carbide. The lapping of the coating on the 600# silicon carbide paper again removed thin layers of material from the nodules before starting to remove material from the main coating.

The conclusion from these observations is that the adhesion of the nodules to the main matrix is excellent and this happens only if the nodule comprises a continuation of the main coating.

The as-deposited surface of the titanium carbide coatings showed a finish which was different from one run to another. Using the TALYSURF-MODEL 3 the measured maximum peak-to-valley roughness was between $2\mu\text{m}$ and $5\mu\text{m}$ and the corresponding centre line average (c.l.a.) values were between $0.32 \pm 0.02\mu\text{m}$ and $0.84 \pm 0.03\mu\text{m}$.

Taking into account the roughness values for the starting surface of the steel substrates which were maximum peak-to-valley roughness of $0.05\mu\text{m}$ and c.l.a. of $0.020 \pm 0.003\mu\text{m}$ it can be said that the used method for titanium carbide coatings does not provide finished surfaces as good as the starting ones.

Finally investigating where the information of the first deposit begins it was found that in the first 5 min. of deposition the round machined edge is covered with the coating material while on the flat well polished part of the cathode-specimen only isolated patches of deposit had appeared Fig.37. The time required to cover the whole surface of the substrate continuously is between 10 min. and 20 min. Taking into account the deposition rates which as mentioned in Chapter 6.4, are between 300 and 400 \AA min^{-1} , it can be seen that between the circumference and the centre of the specimen there should be a difference in thickness of 1000 \AA to 8000 \AA . Differences in thickness of this order are reported in Chapter 6.4.



—17 μ m

Fig. 37 Appearance of the first coating material (black areas) on the flat surface of the specimen after 5 min. of deposition. The grain boundaries of substrate can still be distinguished.

6.2 Adhesion

Samples coated were either evenly covered by the titanium carbide coating or they had patches, mainly around their centre, which had delaminated. This occurred during the cooling period or sometimes during the deposition period. When delamination occurred during the deposition, this caused disturbance of the discharge as already has been mentioned and this could be seen because localised arcing appeared on the surface of the cathode-substrate. It was noticed that delamination was associated with the evenness of transition from the sputter cleaning stage to the actual deposition stage. When the transition was not even, due to improper function of the needle valve which was determining the admission of the carrier gas and the titanium tetrachloride vapour, the result was that suddenly the pressure of the chamber was raised well above the region of glow discharge pressures. It was then necessary to wait for periods of up to 5 min. with the discharge off, until the pressure fell to the level necessary for a stable discharge. During this period of time the ion bombarded surface of the specimen was contaminated again by reabsorbing contaminants from the residual atmosphere. This led to poor adhesion of coating to the substrate.

The results were even worse when deposition of coating material was tried without preliminary sputtering. It was noticed that during deposition the discharge was unstable with continuous arcing and no coating material remained on the substrate during the cooling period. Its fragments were scattered on the chamber pedestal. The same was observed when formation of a graded coating was attempted. The half an hour deposition in the absence of acetylene was followed by 3 hours 10 min. deposition in presence of both reactants. During the latter

period the discharge was unstable and at the end no coating remained on the substrate. Holland⁽⁷⁾ reporting on the contamination of bombarded surfaces cites, that adhesion of evaporated layers to ion bombarded surfaces decreases with the period for which the cleaned surface is exposed in the coating chamber before evaporation. It can be said that the influence of the reabsorbed contaminants in the case of chemical ion plating may be worse than this, because of the higher pressures involved. When only minor difficulties arose during transition from sputter cleaning to the actual deposition with delays of only one or two minutes then recontamination of the bombarded surface was not complete so the deposition proceeded normally without any arcing, throughout the coating period. It was noticed that when spalling occurred it took place during the cooling down period.

The microscopic examination of cross-sections of specimens which were partially delaminated revealed as mentioned in Chapter 5.2.2. that between coating and substrate existed an interlayer apparently different in composition from either of substrate or the coating. Under conditions of excessive recontamination of the substrate the contaminants may intermix with the interlayer material, thus reducing its cohesion and creating a region which is mechanically weak. So, during the deposition period as the coating becomes thicker and as the inherent stresses which are produced during the growth of the coating increase, then spalling will occur if the stresses are sufficient to cause rupture of the interlayer.

If the amount of contamination is smaller, then the failure of the interlayer during the deposition period does not occur. However, the additional stresses arising from the differences in coefficients of expansion, cause spalling of the coating during the cooling period.

It should be noted that when the transition from the sputter cleaning to the deposition was even thus giving minimum opportunity for re-contamination although according to the microscopic examination the interlayer was still present no spalling took place.

Another detail worth mentioning is that coatings deposited from reactants with low concentration of acetylene (up to 15%) did not spall whereas the coatings deposited from higher concentrations of acetylene were always prone to spalling.

Finally it should be mentioned the case of coatings on carburized steel substrates which did not show any spalling effect. In this case no interlayer was observed though small isolated regions of an additional phase could be seen between coating and substrate. Fig.24 Chapter 5.2.2.

Whether the coating was partially spalled off or whether a complete film was present, it was found that it exhibited an ageing effect, as already has been mentioned in Chapter 5.1. After a period of about 24 hours it was possible to start cutting the specimens without any sign of further delamination at the cutting edge. Even lapping of the cross-section of 600# silicon carbide paper, did not cause any detachment of the coating from the substrate. From these details it was inferred that the adhesion of well prepared and aged coatings on the substrates was good.

Other evidence supporting these indications of good adhesion came from the experiments carried out to measure the friction coefficient of the coatings when they were wearing in contact with a rotating

stainless steel counterface. In these experiments it was noticed that the coating wore by a relatively slow asperity cutting mechanism without any sign of spallation or delamination. Holland⁽⁷⁾ writes that when thin vacuum deposited layers are under abrasion pressure their resistance to deformation depends upon the rigidity of the substrate and that other factors affecting the wear resistance are the structure of the film and the degree to which it is bonded to the substrate. So it can be seen that abrasion testing results depend upon the adhesion of the films as well as their hardness and the two factors appear to be inseparable.

Experimental verification of this evidence for good adhesion was carried out by the scratch test which has been developed by Benjamin and Weaver^{(85), (86)}. This technique uses a smoothly rounded stylus which is drawn across the surface of a film under a load which is applied normal to the surface. As the load is progressively increased, a point is reached at which the film is detached by the moving point and the critical load at which this occurs forms a measure of the film-substrate adhesion.

According to the developers of the method the compressive force normal to the substrate causes a plastic deformation of the substrate. This deformation produces a shearing force at the film-substrate interface around the rim of the indentation produced by the point and so a relationship between the applied force and the shearing force exists, so that the adhesion can be calculated as a shearing force.

This theoretical analysis^{(85), (86)} was coupled with experimental results which demonstrated effectively that the critical load

is determined by the characteristics of the film-substrate interface, varying with any change in the one or the other and yet showing no direct correlation with the mechanical properties of either. Furthermore, these investigations have shown that the measured critical load for stripping deposited films becomes independent of film thickness at some critical thickness value ranging from a few hundred to a few thousand Angstroms.

In the current work a series of scratches approximately 2 mm long were made in each film using a modified microhardness tester. Each scratch was made with a different normal load on the Vickers diamond pyramid which had a tip radius of approximately 1 μ m. The critical load, defined as the minimum load at which the diamond pyramid would strip the film cleanly from the substrate leaving a clear channel in the surface, was determined for each film. A typical series of scratches is shown in Fig.38 while in Fig.39 is clearly shown how the coating fails if the used load is above the critical value. The results obtained are given in Table 18 and depicted on the graph in Fig.40. As can be seen from the graph of Fig.40 there is a trend of increasing adhesion with increased carbon content of the coating which in other words means that the critical load has been influenced by bulk film properties, such as film microhardness, in addition to interfacial bonding.

Other investigators reach similar conclusions. Mukherjee et al⁽²⁹⁾ depositing titanium carbide coatings by the sputtering technique found strong dependence of critical load on film thickness of samples which indicated that the critical load was being influenced by bulk film properties, such as film microhardness in addition to interfacial adhesion, since the thickness of the films was well above the critical

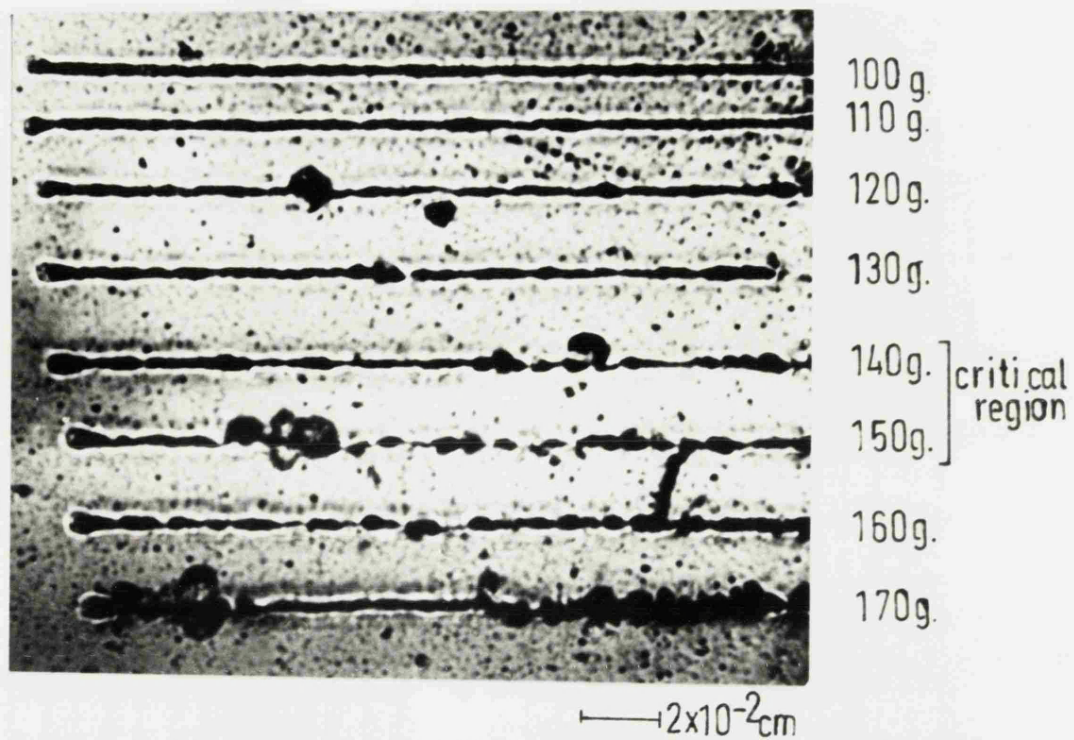


Fig. 38 Estimation of critical load for adhesion

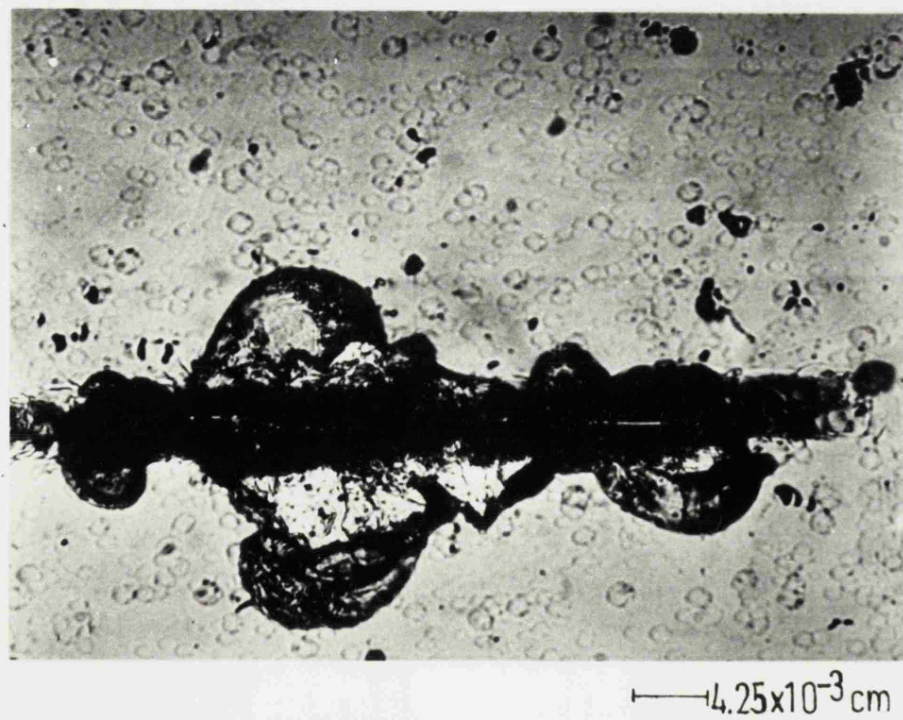


Fig. 39 170g. track showing complete removal of film, exposing the underlying substrate structure

TABLE 18. Adhesion measurements of the titanium carbide coatings produced under different conditions.

Voltage (kV)	Current (mA)	C ₂ H ₂ % in gas reaction mixture	weight % carbon in coating (by EPMA)	Critical load (g)	
				used substrate	
				Mild steel	Carburized steel
4	200	6	37.7	68	90
4	200	9	37.86	72	
4	200	12	43.40	70	
4	200	15	52.94	85	
4	200	18	52.87	184	
4	200	21	61.40	125	115
4	200	24	67.40	-	
4	200	27	64.82	95	
4	200	30	65.10	142	
3	200	21	61.40	92	

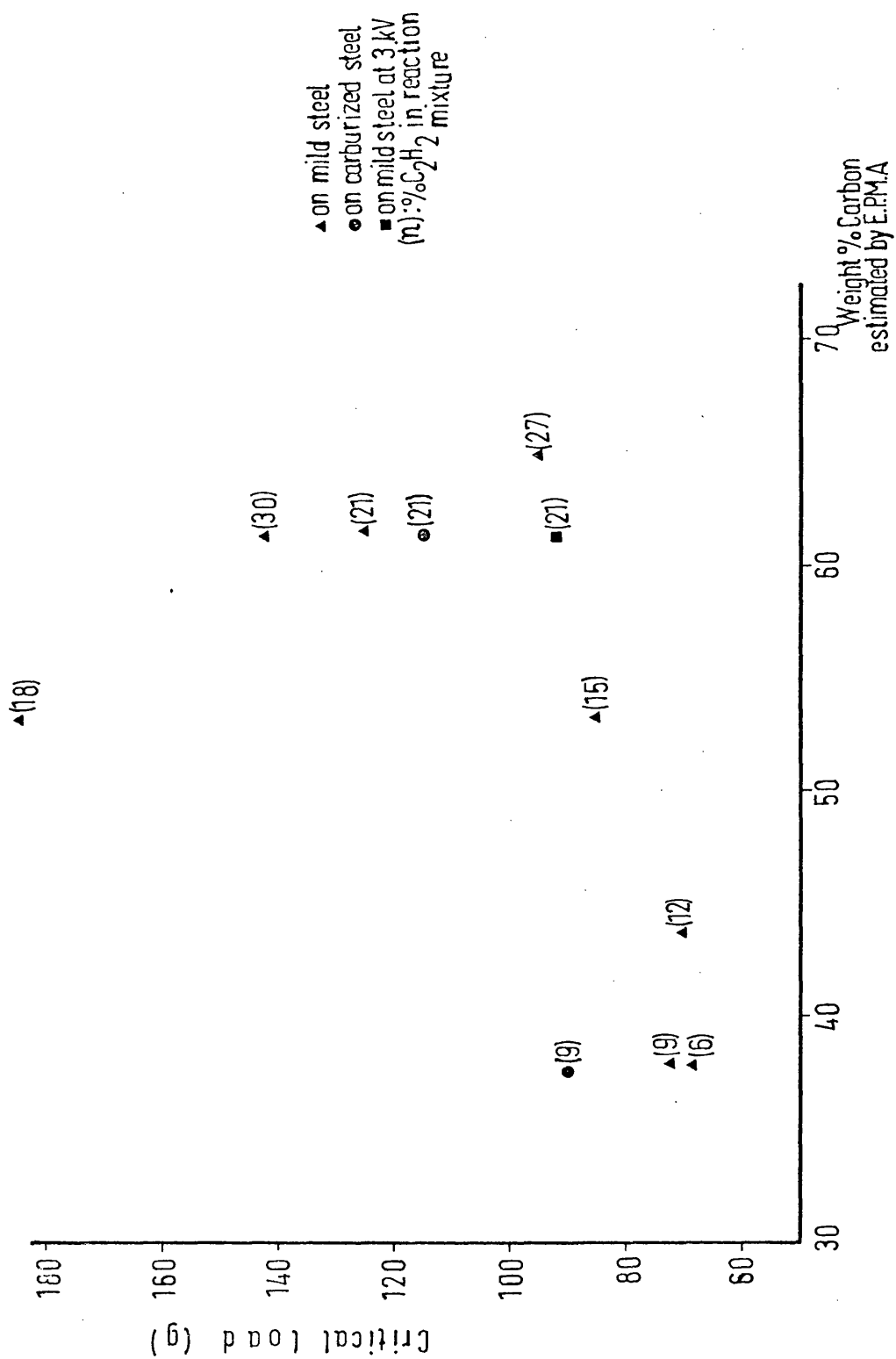


FIG. 40. Critical load as a function of carbon content of coatings prepared under different conditions.

thickness value.

Examining the graph of Fig.40 it can be seen that the value of critical load corresponding to the composition 18% C_2H_2 by volume is exceptionally high in comparison to the values of other compositions and this it is possible to be ascribed to the exceptionally good conditions of deposition and mainly the undisturbed transition from the sputter cleaning to the actual deposition period for this particular sample. This may be considered as an indication of the adhesion quality of the titanium carbide coatings which are possible to be produced by the chemical ion plating when the apparatus is used under ideal conditions of operation.

From the same graph it can be seen that samples produced on the carburized substrates give values of adhesion of the same range as those produced on the mild steel substrates under the same conditions of deposition. However, they have the advantage that they show a lower susceptibility to spalling since they are free of the brittle inter-metallic compounds which are one cause of spallation. On the same graph is given the critical load corresponding to the coating deposited at the conditions: voltage 3kV, current 200 mA and composition of gas reactants 21% C_2H_2 by volume. It can be seen that its value is approximately 40% smaller than that for the corresponding coatings deposited under the same conditions but at higher potential (4 kV). This agrees with theories of ion plating which say that the bond strength between coating and substrate increases with the increase of the substrate potential. (9), (52), (53)

6.3 Microhardness

The as-deposited coatings were not suitable for microhardness measurements due to the topography of their surface. Using the Vickers microhardness tester on a M 12a microscope and loads below 20 g the indentations could not be seen because of the surface roughness (Chapter 6.1). Using loads of 50 g indentation marks could be seen but the perimeter of the indentations and their diagonals were not easily defined. Using loads of 100 g or more, due to the soft mild steel substrate beneath the titanium carbide, the coating yielded, cracking in a circular mode around the point of application of the load.

So in order to take the hardness measurements of the titanium carbide coatings some preliminary preparation steps were taken. First the sample was mounted and then polished. Care was taken so that the polishing was stopped when the surface of the sample examined under the optical microscope showed that the bulk of the nodules had just been removed. At this point there was the certainty that the bulk thickness of the coating was intact.

For the coatings with relatively low hardness this polishing took place directly on polishing cloth with 1 μm diamond paste. For coatings with hardness above 2300 kg mm^{-2} it was necessary to lap them on a 600# silicon carbide paper before passing onto the polishing cloth. A mirror polished surface was necessary for accurate hardness measurements.

It was found that the samples with hardness below 2300 kg mm^{-2} , when tested with load of 50 g yielded with a characteristic circular

mode. Consequently all measurements were recorded using a 20 g load. Although, the square perimeter of the indentations was not well defined due to their shallow depth, however, their diagonals could be seen as a dark cross when the level of illumination was reduced.

For each sample 20 readings were taken, and these always showed a considerable scatter. Typical standard deviations were 235 V.P.N.

A problem which may arise with microhardness measurements of thin films is that the diamond may completely penetrate the coating. The depth of a Vickers hardness impression is always 0.143 of the diagonal length. Thus using a 20 g load, a 1000 V.H.N. impression would penetrate film of 0.87 μm and a 3000 V.H.N. will only penetrate 0.5 μm . As can be seen in table 19 all measured coating were substantially thicker than these values.

In the same table were listed the mean values of the microhardness measurements and their standard deviations for different titanium carbide coatings obtained under stable ion plating conditions i.e. voltage 4 kV, current 200 mA and deposition time 3 hours 10 minutes. The substrates used were mild steel of 0.25% C except for two experiments carried out using carburized steel substrates. Also in the same table the data for coatings produced at 21% carbonaceous gas in reaction mixture with the same current and deposition time as the above mentioned but at voltages 3 and 5 kV are given. While satisfactory hardness measurements could be made on the first of these films the second was too thin to allow measurements. Finally the measurements for the coatings produced at 30% carbonaceous gas in the reaction mixture, under the conditions of voltage 4 kV, deposition time 3 hours 10 min. and varied currents are given.

TABLE 19. Microhardness of the titanium carbide coatings produced under different conditions, using load test of 20 g.

Voltage (kV)	Current (mA)	C ₂ H ₂ % in gas reaction mixture	weight % carbon in coating (by EPMA)	Thickness (μm)	Microhardness kg mm ⁻²	
					Used substrate	
					mild steel	carburised steel
4	200	6	37.70	5.90	853 + 60	1439 + 237
4	200	9	37.86	6.70	1641 + 253	
4	200	9	37.86*			
4	200	12	43.40	5.50	2294 + 365	
4	200	15	52.94	6.85	2546 + 246	
4	200	18	52.87	7.45	2826 + 305	
4	200	21	61.40	7.46	2851 + 342	
4	200	21	61.40*			2889 + 276
4	200	24	67.40			
4	200	27	64.82	10.63	2885 + 195	
4	200	30	65.1	13.60	3026 + 206	
3	200	21	61.40*	5.10	2553 + 283	
5	200	21	61.40*	1.70	no measurement obtained due to very thin film	
4	80	30	65.1*	4.70	1425 + 110	
4	100	30	65.1*	2.85	1688 + 190	
4	120	30	65.1*	3.25	1761 + 212	
4	160	30	65.1*	8.50	2331 + 224	
4	200	30	65.1*	13.60	3026 + 206	

*Estimate based on the specimens deposited on mild steel under the same conditions.

These results are depicted on the graphs of Fig.41 and Fig.42. As can be seen from the graph of Fig.41 the microhardness up to 18% carbonaceous gas concentration increases sharply as the hydrocarbon concentration in the reaction mixture increases. Above this concentration the hardness tends towards a limiting value of approximately 2900 kg mm^{-2} . This coincides with the findings of Lee and Richman⁽³²⁾ who have deposited titanium carbide on cemented carbide substrates by the chemical vapour process. Similar conclusions were reached by Elyuting et al⁽³³⁾ who have deposited titanium carbide coatings onto the refractory metals tungsten and molybdenum. The first two investigators try to give also an explanation of the causes for the variation in hardness as a function of the hydrocarbon concentration in the reaction mixture. They report that since oxygen and nitrogen concentrations, which otherwise could affect the hardness, were carefully controlled the remaining factors are as follows:

- a) when the hydrocarbon concentration in the coating system is high, the degree of supersaturation and therefore the nucleation rate increases. The coatings deposited under these conditions would have a finer grain size than coatings deposited under other conditions.
- b) titanium carbide usually has some carbon deficiency (as compared to its stoichiometric composition) and the hardness of the carbide increases linearly as the carbon deficiency decreases. So in order to deposit a strong and hard continuous film, the coating system must provide the needed high degree of supersaturation.

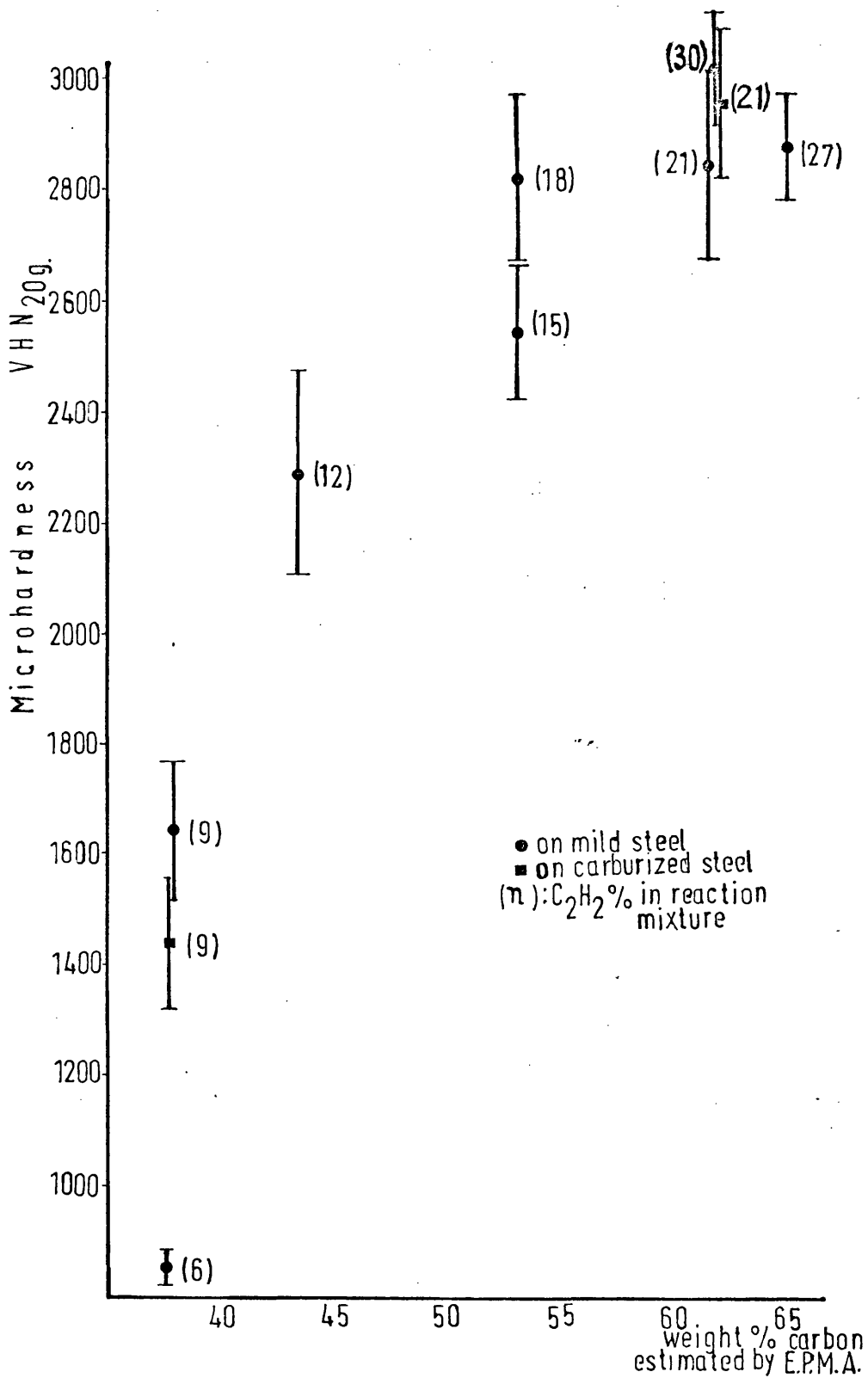


FIG. 41. Microhardness of Titanium carbide coatings of different carbon contents produced under conditions: voltage 4kV, current 200mA, and different compositions of gas reactant.

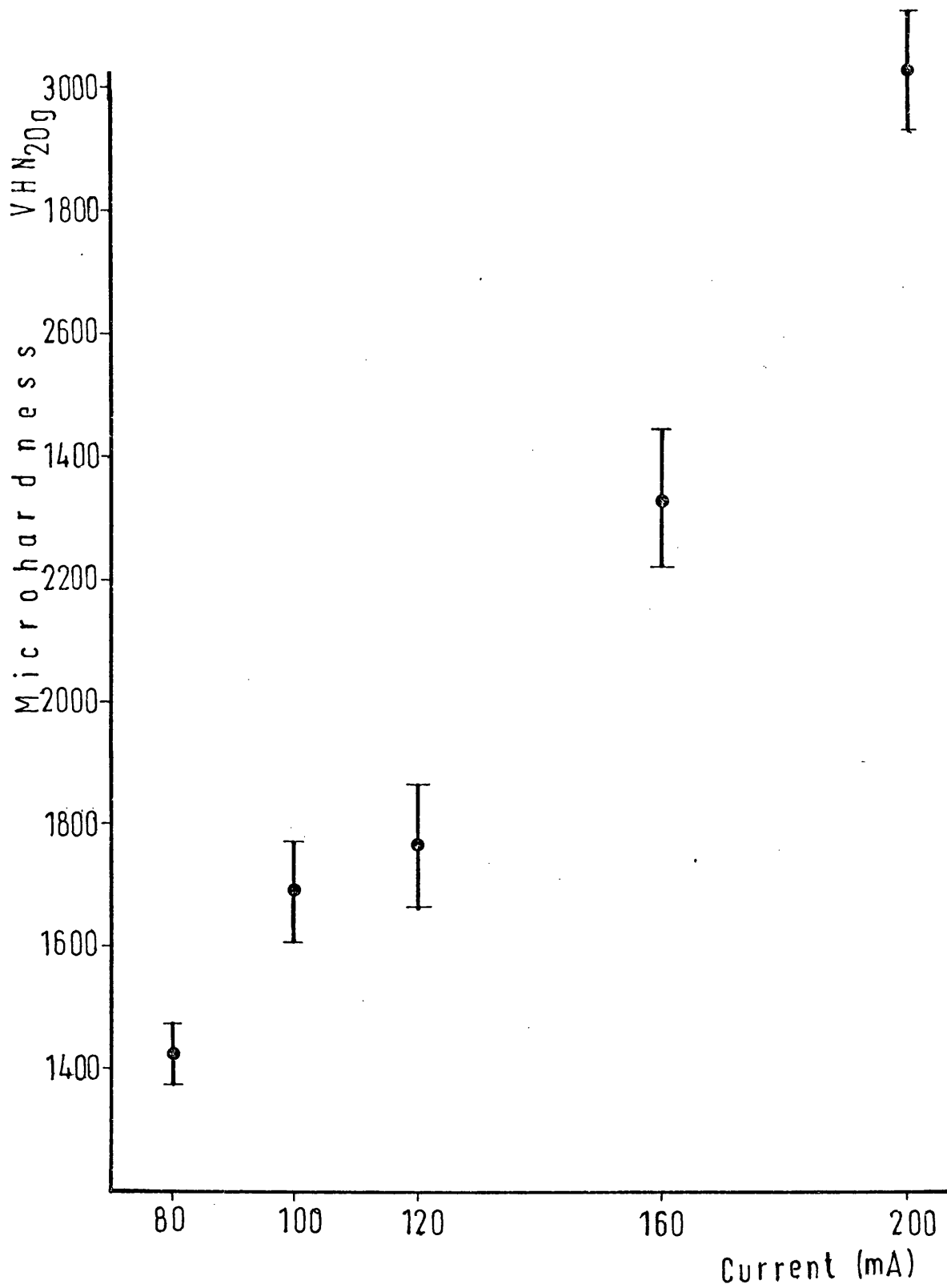


FIG. 42. Microhardness of titanium carbide coatings at different glow discharge currents.

If this explanation is applied to coatings prepared by chemical ion plating then it would appear that supersaturation of the gas mixture with acetylene occurs at composition of about 18%.

As it can be seen in graph of Fig.41 in addition to the hardness values given for coatings on the mild steel substrates, there are also given two values of hardness of carburized steel. These two experiments were carried out to investigate the influence of the substrate on the properties of the coatings. Elyuting et al⁽³³⁾ report that for the same thickness titanium carbide coatings prepared under the same conditions on tungsten and molybdenum showed that the coating on tungsten was harder than that on molybdenum. This is ascribed to the effect of substrate hardness material (520 kg mm^{-2} for tungsten and 240 kg mm^{-2} for molybdenum). Archer⁽⁴⁵⁾ reports that the hardness of the coating must match, to some extent, the hardness of the substrate. A very soft substrate beneath a hard coating will yield under load and lose the advantage of the outer hard coating. Tungsten carbide (of hardness greater than 2000 V.P.N.) on tool steel (about 500 V.P.N.) gives a surface which is almost entirely scratch-proof, but the same coating on a low carbon steel (about 200 V.P.N.) is scratched quite easily. On the same subject White⁽⁶⁾ is more definite and recommends a Knoop hardness ratio of 2/1 as a maximum between substrate and coating.

On this basis, because the mild steel used had a hardness of only 270 kg mm^{-2} and the coatings were well above 2500 kg mm^{-2} there was a hardness ratio of about 9/1 so carburized steel, prepared as described in Chapter 5.1. having a hardness of about 950 kg mm^{-2} , was used to

to approach the recommended low ratio. However, no significant change in hardness of these coatings compared to those prepared under the same conditions was observed, though the bonding to these substrates was excellent.

From the graph of Fig.42 it can be seen that the hardness values increase with increase of the glow discharge current. This can be ascribed to the influence of the power dissipated at the substrate to each particular current value. This influences substrate heating by the ionic bombardment which takes place during the preliminary sputter cleaning and also during the actual deposition stage. From the evidence which exist such as depth of decarburization of the substrate, crystallinity of deposits it can be concluded that at higher currents, higher temperatures are reached. The influence of the substrate temperature on the microhardness of titanium carbide coatings produced by activated evaporation was investigated by Raghuram and Bunshah⁽³⁴⁾ and they reached to the conclusion that both diamond pyramid and Knoop hardness values increase with increase is substrate temperature.

6.4 Thickness Measurements and Uniformity of Deposits

For measuring the thickness of the deposited coatings metallographic cross-sectioning was used. As it was mentioned in Chapter 5.2.2 the other purposes of this were to investigate the structure of the coating and presence of defects. The preparation of the cross-sections, is described in detail in Chapter 5.2.2. Care was taken for the cross-section to be normal to the surface so that errors in misalignment were less than 5° . These cross-sections were etched in 2% Nital and thus the boundary of the coating with the substrate was clearly defined.

The specimens prepared for this purpose were examined at 400 times magnification along the whole length of the section and this showed that the coating thickness was uniform. In order to measure the exact thickness of the coatings, photographs were taken of two separate areas for each particular sample at 2100 times magnification. The magnification was checked with a stage micrometer. A typical picture is given in Fig.25 (Chapter 5.2.2). The mean thickness measurements were taken at 20 different points on the same picture. It is estimate that the systematic errors due to specimen fit and other sources are less than 10%.

To investigate the relation between thickness of the coatings and the deposition time, four samples were prepared under the conditions of voltage 4 kV, current 200 mA, composition of gas reactants 30% C_2H_2 by volume. The results of this series of experiments are illustrated on graph of Fig.43. It can be seen that there is a linear relation between coating thickness and the corresponding deposition time. Such a relation found also in other methods as, in C.V.D.⁽⁴¹⁾ by which titanium carbide coatings were prepared, and in electrodeless

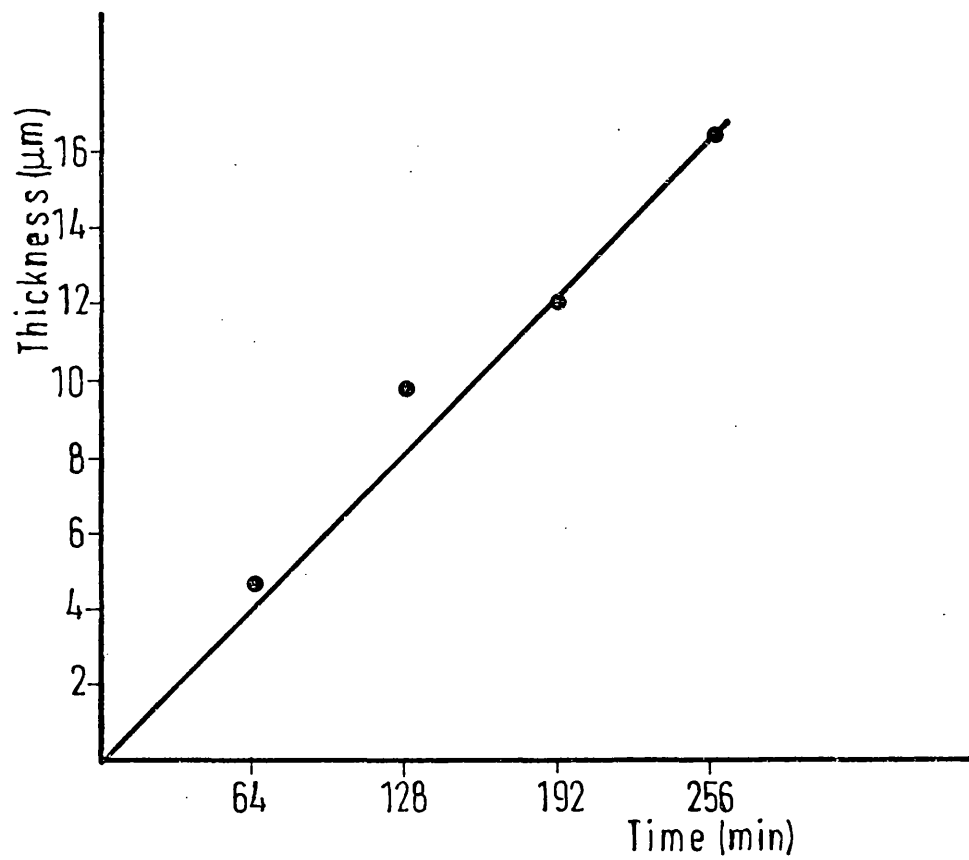


FIG. 43. Variation of coating thickness as a function of deposition time.

R.F. discharge⁽⁶⁷⁾ by which silicon oxide was deposited. Subsequently all experimental runs, which carried out to investigate the influence of other parameters on film thickness and properties lasted for 3 hours and 10 minutes.

The thickness of coatings deposited under the same glow discharge conditions but different composition of gas reaction mixtures was measured. The mean thickness measurements obtained as mentioned above, are tabulated on Table 20 and illustrated on graph Fig.44. As can be seen from this graph there is a trend of thickness increase as the amount of hydrocarbon increases. This seems also to be the case in the investigations of Elyutin et al⁽³³⁾ who found that under the same deposition conditions the thickness of coating increases as the amount of hydrocarbon in the reaction mixture increases. Hintermann and Gass⁽³⁰⁾ using the C.V.D. method have found that the thickest coatings were obtained with the lowest titanium tetrachloride concentration. Finally, Lee and Richman⁽³²⁾ using the C.V.D. method as well, have found that film growth rate increases with increased hydrocarbon content of the reactant gas mixture. Coatings deposited on the carburized steel substrates had a thickness approximately equal to those deposited on mild steel under the same conditions.

Coatings deposited on mild steel at 3 kV and 5 kV were thinner than that deposited at 4 kV with all other conditions remaining the same. The reason is that at 3 kV the efficiency of the reaction is not as good as at 4 kV due to lower dissipation of energy on the substrate, while at 5 kV the rate of sputtering probably increased and this can be seen by the increased surface etching on this specimen. The thickness of coating prepared in presence of only titanium tetrachloride at voltage 4 kV, current 200 mA and deposition time 4 hours

TABLE 20. Thickness in μm of titanium carbide coatings produced under glow discharge currents of 200 mA, different voltage values and deposition time, 3 hours and 10 minutes

Used substrate	Voltage (kV)	C_2H_2 % in gas reaction mixture	Thickness μm (Mean of 20 readings)		
			Overall mean value	Edge	Centre
Mild steel	4	6	5.90 \pm 0.45		
Mild steel	4	9	6.70 \pm 0.52		
Mild steel	4	12	5.50 \pm 0.42	5.67 \pm 0.49	5.33 \pm 0.31
Mild steel	4	15	6.85 \pm 0.60	7.26 \pm 0.74	6.44 \pm 0.50
Mild steel	4	18	7.45 \pm 0.62	7.50 \pm 0.45	7.40 \pm 0.70
Mild steel	4	21	7.46 \pm 0.57		
Mild steel	4	24			
Mild steel	4	27	10.63 \pm 0.59		
Mild steel	4	30	13.60 \pm 0.55		
Carburized steel	4	9	6.1 \pm 0.60		
Carburized steel	4	21	8.5 \pm 0.52		
Mild steel	3	21	5.1 \pm 0.50		
Mild steel	5	21	1.7 \pm 0.30		

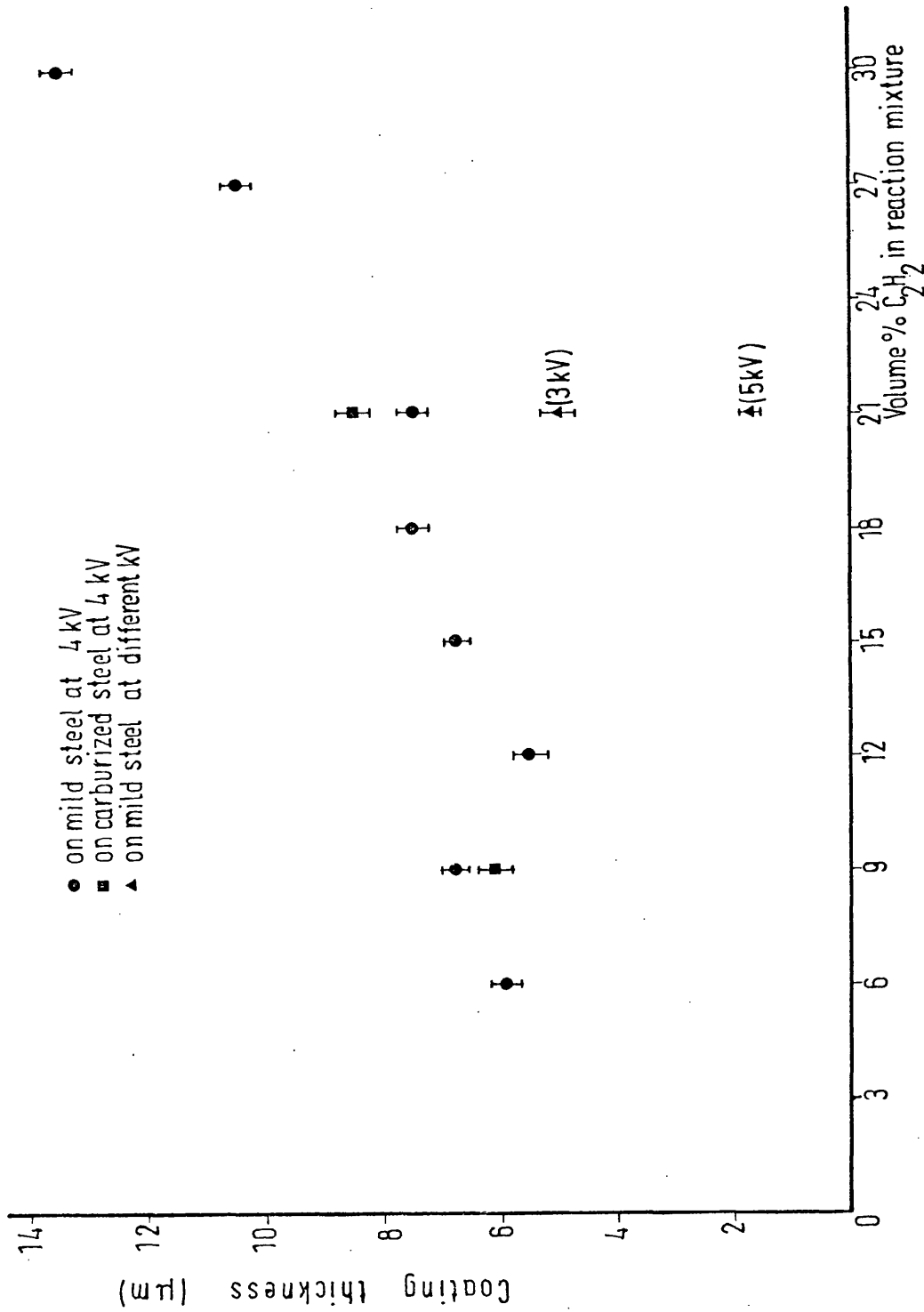


FIG. 44. Variation of coatings thickness as a function of acetylene in the reaction mixture.

was only $0.9\mu\text{m}$.

Considering the deposition rates obtained in the series of experiments at voltage 4 kV it can be seen that these changes between $1.70\mu\text{m h}^{-1}$ and $4.30\mu\text{m h}^{-1}$ (thickness over the deposition time). From this it can be seen that the rates obtained are much higher than those by sputtering⁽³⁷⁾ of the same material which is only $0.095\mu\text{m h}^{-1}$ and in the same range as those by chemical vapour deposition ($1-10\mu\text{m h}^{-1}$ (36) and $0.5-0.9\mu\text{m h}^{-1}$ (30)).

As mentioned in Chapter 6.1 deposition starts on the round edge and its vicinity and proceeds towards the centre. The complete covering of the specimen surface takes 10 - 20 min so there is a thickness difference between the circumference and the centre of the specimen of about $0.5 - 1.0\mu\text{m}$. This was confirmed by more extensive measurement on certain samples shown in the final columns of Table 20.

The "throwing power" of the method was investigated by using a perforated specimen with through or blind holes of different diameters. Good "throwing power" was illustrated by formation of coating even on the walls of a blind hole, 1.5 mm in diameter, at a distance of approximately 1.50 cm from the edge of the specimen. The measured thickness at this point was approximately $2\mu\text{m}$, while the thickness of the coating on the flat surface was $16\mu\text{m}$. Thickness of coatings in other places lay between these two values. Fig.45 illustrates the substrate and the points at which thickness measurements were taken. The values obtained are also cited. The picture of Fig.46 shows the coating obtained at point J.

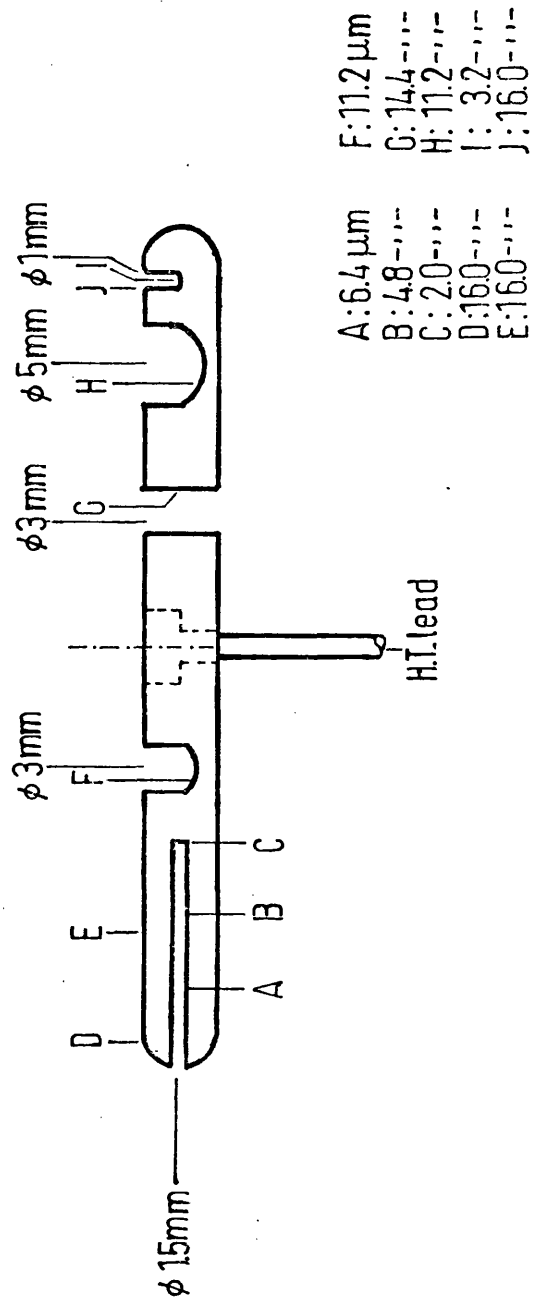


FIG. 45. Schematic diagram of the perforated substrate used to investigate the "throwing power" of the chemical ion plating method.

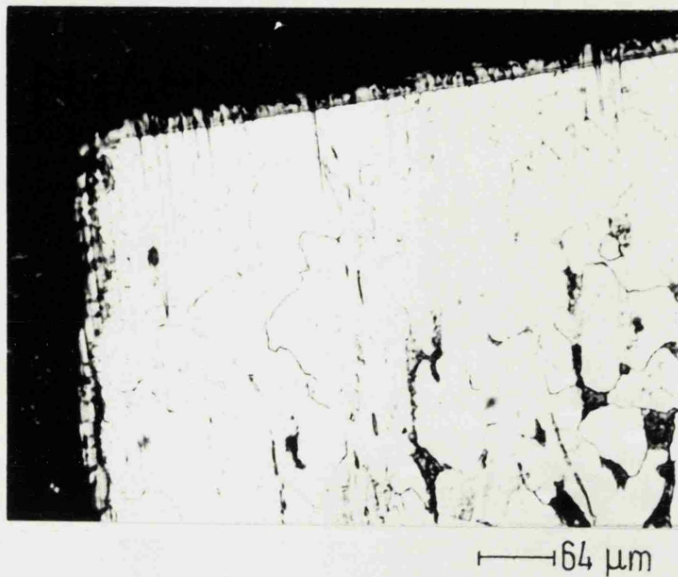


Fig. 46 Uniformity of coating of titanium carbide around a corner and into a blind hole of diameter 1mm on a mild steel substrate

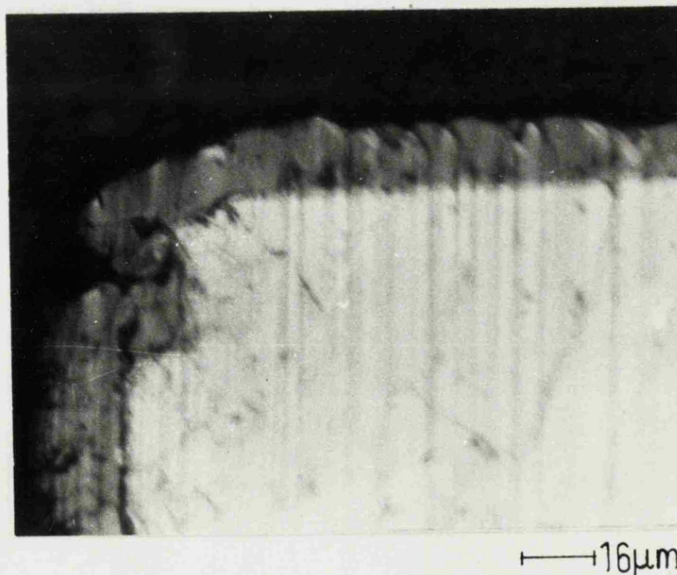


Fig. 47 The corner of Fig. 46 showing coating uniformity around it and absence of build-up

The cylindrical specimens prepared under the conditions mentioned in Chapter 5.1 (Table 13-d₂) were uniformly coated around their surfaces except along the region facing adjacent samples. This could have been due to electrical field distortion.

Finally, it should be mentioned that this method did not show any build-up of coatings at corners of specimens. This can be seen in Fig.47.

6.5 Friction and wear

The wear resistance characteristic of refractory compounds are well known and many investigations have been carried out with the purpose of using such compounds in the form of coatings on different substrates. Amongst such refractory compounds, titanium carbide has been one of the best candidates for coatings for wear resistant applications. Vapour deposition methods are commonly used for preparing such coatings and chemical vapour deposition is the usual one. The most important practical application of titanium carbide coatings is the coated inserts used for machining purposes. The idea of coating tools with titanium carbide is about 15 years old. However according to Ljungqvist⁽³¹⁾ the great practical application came with the introduction of the "throwaway" inserts. In this case the method of coating does not permit regrinding or brazing of the tip.

Basic factors which determine the mode of wear of a coating are first the coating-substrate adhesion and second the friction between the coating and the material with which it is coming in contact when the coated part is used for machining purposes.

With poor adhesion, a coating may not wear by the normal, relatively slow, asperity welding mechanism, but the high-rate mechanisms associated with spallation and delamination. Moreover, the relatively large particles formed by spallation of a poorly adherent hard coating could act in an abrasive manner and, in fact, accelerate the wear of the surface it was intended to protect.

The adhesion of coatings prepared by chemical ion plating is good

as can be inferred from the description given in Chapter 6.2. The same conclusions were obtained when the friction coefficient value of titanium carbide coating against stainless steel counterface was measured. The samples examined under the microscope after their friction tests, showed no sign of detachment of coating material and it was revealed that the wear was progressing by removing material of thin layers parallel to the counterface surface. Even the nodules which protrude above the main titanium carbide matrix, and which during the first stages of a friction measurement are under high stresses because of the restricted contact area, wore in the same way without any sign of detachment. Details are given in Chapter 6.1.

The friction measurements on the samples were carried out on a modified pin and disc machine. The sample in the form of a 1.25 cm diameter flat disc which was coated according to the details given in Chapter 5.1 was pressed down against the counterface by a holder, as it can be seen on Fig.48 mounted in a linear motion bearing, which allowed free vertical movement to counteract unevenness of the metal counterface and permitted contact to occur over the biggest possible area. To avoid rotation of the sample around its central vertical axis, apart from the central supporting pin between holder and sample a second pin was placed in an off-centre position as can be seen in Fig.48, and thus the same area of specimen was continuously in contact with the rotating counterface.

The sample holder accommodated a weigh holder on which a normal load of 13 N was applied.

The specimen holder and linear bearing was fixed to a long, mild

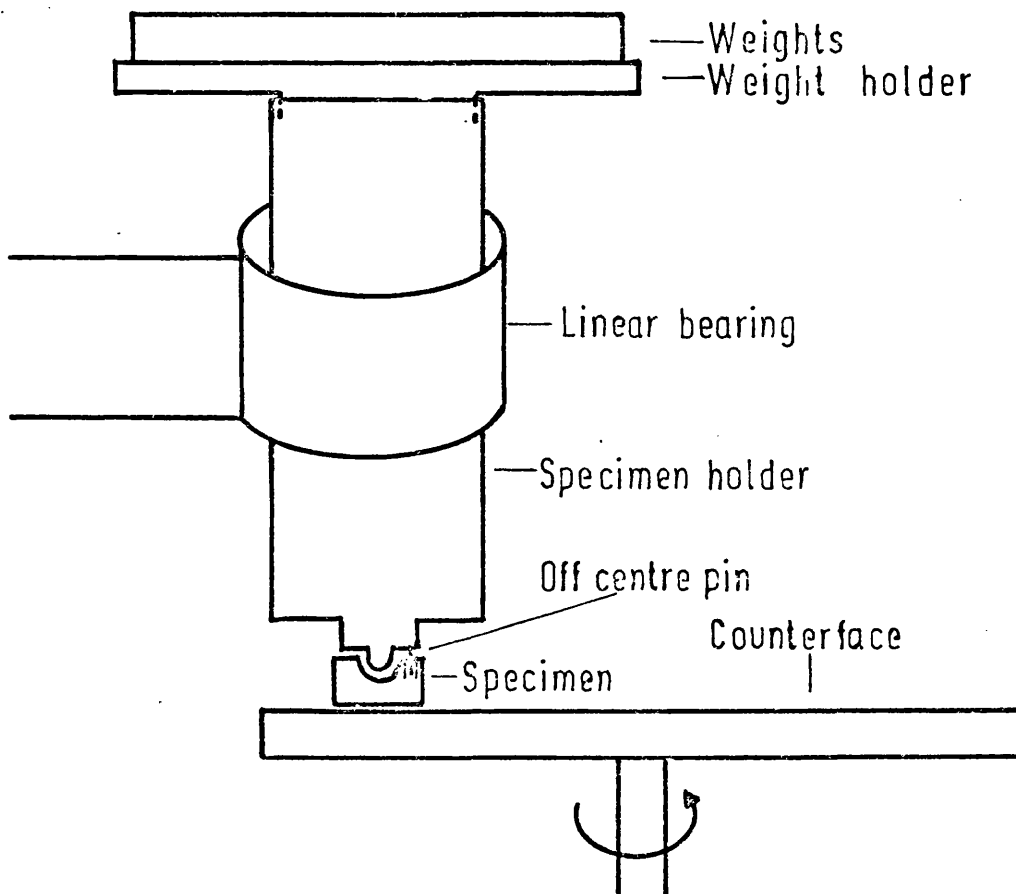


FIG. 48. Schematic illustration of the arrangement between specimen holder-specimen-counterface used to measure the friction coefficient.

steel beam which was deflected by the frictional force between the rotating counterface and the immovable sample. This deflection was monitored by strain gauges, the signal was amplified and then recorded with a standard chart recorder. From these readings the dynamic friction coefficient was calculated.

The counterface used a stainless steel disc of 10 cm diameter and of 310 kg mm^{-2} hardness, was always polished by means of $1 \mu\text{m}$ diamond paste prior to each run. The roughness of the polished counterface was measured using the TALYSURF-MODEL 3 and the centre line average (c.l.a.) was $0.020 \pm 0.002 \mu\text{m}$. The speed of its rotation and the applied normal load were kept constant during the whole series of experiments, at 2 rpm and 13 N respectively. Under these conditions the wear between sample and counterface was smooth and the value of the frictional force obtained was constant at the first stages of the experiment. However, due to the high hardness of titanium carbide surface, rubbing in contact with a relatively soft counterface, grooves formed on the counterface from the first revolution. This was the result of a ploughing effect of the hard titanium carbide protrusions which were in actual contact with the counterface. As the experiment was extended, debris from the counterface material and the worn parts of the titanium carbide surface layer was accumulated besides the grooves and so the counterface gradually became rougher. The result was that the measured frictional force gradually increased from typically 2.50 N to 4.50 N after 50 revolutions.

The samples used for the measurements of the coefficient of friction were produced under the ion plating conditions of 4 kV voltage and 200 mA current at four different compositions of the mixture of the gas

reactants. These compositions were 9%, 15%, 21% and 30% in C_2H_2 . The number of samples produced during each of these runs was six. The measured coefficient of friction varied between 0.18 and 0.28, as can be seen from the Table 21.

The values of coefficient of friction of titanium carbide against steel given by literature are: 0.14-0.15 according to Arnstein⁽³⁶⁾ and 0.25 according to Muckherjee et al⁽²⁹⁾. It can be seen that the values obtained by chemical ion plating fall within the range of 0.14-0.25 given by the literature.

Commenting on the results in Table 21 it can be said that the values obtained for the coefficient of friction depend on the surface preparation of the counterface and the samples. It seems, however, that the lower values of friction coefficient correspond to high concentrations of acetylene in the reaction mixture and conversely the higher values correspond to low concentrations of acetylene. This may be connected with the hardness of the coatings, since as can be seen from the Chapter on microhardness 6.3, at high concentrations of acetylene in the reaction mixture correspond high values of hardness.

Finally, taking into account the low coefficient of friction values and the good adhesion of the titanium carbide coatings on steel substrates, obtained by chemical ion plating it can be concluded that this method may provide a good answer to problems related with wear.

TABLE 21. Dynamic coefficient of friction of titanium carbide coatings against stainless steel counterface.

(Deposition conditions : voltage 4 kV, current 200 mA)

Carbonaceous gas (%) in reaction mixture	Measured values of coefficient of friction						Average values
9%	0.26	0.26	0.21	0.28	0.24	0.22	0.24
15%	0.27	0.23	0.26	0.25	0.20	0.25	0.24
21%	0.22	0.18	0.28	0.22	-	0.27	0.23
30%	0.23	0.18	0.20	-	0.23	0.21	0.21

CHAPTER 7

DISCUSSION AND CONCLUSIONS

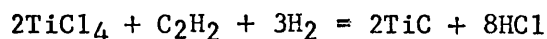
The results of individual analytical processes and measurements have been discussed already in the appropriate chapters; therefore this final chapter seeks to bring these conclusions together so that the reader may consider the method and its results in an independent, concise way.

Titanium carbide coatings on different substrates, as mentioned in Chapter 1.3, can be prepared by different vacuum deposition methods such as activated reactive evaporation, sputtering or usually by chemical vapour deposition. However the ion plating techniques (conventional and reactive) which are succesful in depositing other materials (metals or compounds) does not seem to be succesful in depositing titanium carbide coatings. The reason is the high melting point of titanium carbide (3,067 °C) and also that under vacuum it dissociates to carbon and titanium below its melting point. Thus the material is unsuitable for conventional ion plating. Reactive ion plating as tried by Stowell⁽⁸⁾ gave a soft codeposited mixture of carbon and titanium and not a hard stoichiometric compound which is dense and adherent as can be expected when ion plating is used. The reason that the material does not react, seems to be lack of activation energy required, which would make the codeposited species react, giving crystalline coatings. Since codeposition of carbon and

titanium has occurred the fact that no reaction occurred must imply lack of thermal energy on the substrate surface. Because the only way of heating the substrate was by ion bombardment, it maybe deduced that the power dissipated at the substrate surface was insufficient to provide the required activation energy. This also was the case during the early part of the present investigation when deposition by chemical ion plating was carried out at low current densities (less than 2mAcm^{-2}). The coatings formed were a codeposited, unreacted mixture of titanium, carbon and chlorine. On the other hand the information given by Bunshah⁽³⁴⁾ and co-workers, depositing titanium carbide by activated reactive evaporation in a similar set up as used by Stowell, but heating the surface independently, showed that the lattice parameter reaches the values characteristic of stoichiometric composition at substrate temperatures between 720 and 1450°C, while at low temperatures (520-610°C) reaches the lattice parameter value of a substoichiometric composition. This leads to the conclusion that for the formation of crystalline titanium carbide the substrate temperature is of vital importance.

In the present investigation the deposition of titanium carbide coatings from gaseous reactants by the assistance of glow discharge (chemical ion plating) is feasible under conditions of high voltage (3 to 5kV) and high current densities ($3.33\text{--}5.00\text{mAcm}^{-2}$). Under such conditions the power dissipated during the sputter cleaning

and deposition periods heats the cathode-specimen to temperatures between 500°C and 600°C. In this temperature range the activation energy thermodynamically needed for the start and completion of the reaction



can be provided and thus titanium carbide coatings can be obtained. The need of a relatively high substrate temperature for the formation of the coatings implies that the reaction takes place on the surface. If this was not the case and a homogeneous reaction could take place in the gas phase some of the formed compounds could form agglomerates big enough to be charged negatively, as explained in Chapter 3.1. and thus these would deposit on anodic parts of the system. However anodic coatings of titanium carbides were never observed. Another reason supporting this supposition is that a homogeneous gas reaction between excited molecules requires collision with a third body in order to dissipate the excess energy. Since three body collisions are approximately 1000 times less frequent than two body collisions⁽⁸⁷⁾ then the rate of this homogeneous gas reaction will be low.

The coatings obtained analysed by X-ray diffraction showed only the characteristic pattern of titanium carbide and no additional lines corresponding to any other crystallographic forms. The X-ray diffraction pattern proved to give a lattice parameter of mean value $4.347 \pm 0.009 \text{ \AA}$ which is higher than that accepted for titanium carbide ($4.328^{(27)}$ or $4.33 \text{ \AA}^{(72)}$). The shifting towards these high values of the lattice parameter can be ascribed, as

mentioned in Chapter 5.2.1, either to the presence of chlorine dissolved in the lattice or to microstresses accumulated in the grains of the material during the deposition . At low current densities below 2mAcm^{-2} the material deposited was amorphous to X-rays. At higher current densities the lines on the Debye-Scherrer films corresponding to titanium carbide were distinguishable from the background but they showed marked line broadening. Because of this evidence it can be concluded that the deposited material is very fine grained (smaller than 1000 \AA).

The qualitative analysis by electron probe microanalysis showed that the coatings consist of titanium, carbon and chlorine. Oxygen which is usually a common impurity in titanium carbide prepared by methods like sintering was not detectable in the coating prepared by the process followed in the present investigation.

The quantitative analysis by the same method showed that the coatings consist of chlorine 3.5- 4.0% by weight, titanium 30-59% by weight and the remaining is considered to be carbon content which varies between 38 and 67% by weight. A chemical analysis of three samples gave carbon content in the same range. It can be seen that the carbon content is higher than that for stoichiometric composition which is 20% by weight. This excessive amount of carbon must exist as a second phase, since the solid solubility of carbon in titanium carbide is normally very small 1.5-2%^(8,29). However this

could not be detected by the methods available and the implications are as follows:-

- a) the carbon is in an amorphous, non-graphitic form because it was not detected by X-ray diffraction.
- b) that the grain size is smaller than 1000 \AA because it was not possible to resolve it by scanning electron microscopy or electron probe microanalysis (taking X-ray pictures) due to the inherent instrument limitations and the nature of the specimens.

Considering the evidence from X-ray diffraction and electron probe microanalysis it can be said that the coatings obtained contain titanium carbide, chlorine and free carbon. The shifting of the titanium carbide lines on the Debye-Scherrer films indicate that this material is under a considerable strain. This is either due to the stresses accumulated between its grains during deposition or due to chlorine atoms which occupy some of the octahedral sites in the unit cell of the titanium carbide. The ratio of the atomic radii of chlorine and titanium is 0.67. According to Hägg rules when this ratio is greater than 0.59 the obtained unit cells are complex. In the present case the obtained unit cell remains simple (fcc) corresponding to titanium carbide structure because maybe the amount of chlorine (approximately 4% by weight) is not high enough to cause complete change of the unit cell. However this maybe sufficient to distort the unit cell causing additional

interstitial sites so more carbon maybe dissolved. If this happens it can be accepted that the incorporation of chlorine in the unit cell of titanium carbide creates a number of defects causing loosening of its cohesion and this is counterbalanced only when the required amount of carbon occupies the sites created.

The microscopic examination of cross-sections of the coatings showed that when mild steel was used as substrate there was always an interlayer of about $1\mu\text{m}$ thick between the coating and the substrate. This interlayer can be considered to be an intermetallic of the form FeTi or Fe_2Ti as explained in Chapter 5.2.3. This interlayer seems to be detrimental to the adhesion of the coatings because it causes spallation of the deposited material. In the case of carburized steel substrates this interlayer either does not exist or it is isolated and discontinuous along the interface. These coatings showed no sign of spallation. Underneath the interlayer in the cases of the mild steel substrates there is always a decarburized zone of approximately $90\mu\text{m}$ which is created by thermal diffusion and ionic bombardment during the preliminary sputter cleaning period. It does not extend further during the deposition period. In the case of the carburized steel substrates this effect does not seem to be so prominent. This is because in a carburized substrate the diffusion of carbon is slower due to different structure and because the amount of carbon which must be removed is much greater so a pure ferritic surface is unlikely to be formed in the time available. Thus the presence of iron carbide on the surface acts as an inhibitor to the formation of this intermetallic compound.

To find the texture of coatings, if any, and reveal the grain size, samples were polished and exposed to a number of etchants known to be effective to coarse grained titanium carbide. However none of the reagents tried, gave satisfactory answer to this problem. This leads to the conclusion that the material had no texture and that it is dense with very small grain size (below 1000\AA). As such it was impossible to be resolved by optical and even scanning electron microscopy at high magnifications. This evidence is compatible with the same conclusion obtained by the X-ray diffraction investigation. Furthermore the examination of the coatings cross-sections showed that they had no gross internal defects like porosity or cracks, they were dense and they had no preferred orientation.

The thickness of coatings prepared under the same conditions of glow discharge and for the same deposition time but with different concentration of reactant mixtures changed from approximately $5.5\mu\text{m}$ at low concentrations of acetylene to $13.6\mu\text{m}$ at high concentrations of acetylene. It has also been shown that the deposition of coatings increases linearly with time. So it can be seen that the deposition rate changes from 1.70 mh^{-1} to 4.30 mh^{-1} . From these figures it can be said that the deposition rate of the method is higher than the corresponding to deposition of the same material by sputtering⁽³⁷⁾ or in the same range as that for chemical vapour deposition^{(30), (36)} but is much lower than the deposition rates obtained by conventional and reactive ion plating when simple metals or compounds are deposited. This could be ascribed to the

fact that the carrier gas did not become saturated with titanium tetrachloride, so the reagents were not present in stoichiometric proportions. As a result the vapour reaction mixture contained excessive amount of acetylene.

This method, as was expected from literature on ion plating provided very good uniformity of coatings and no coating build-up on corners. Coating was deposited evenly on the walls of a blind hole, 1.5mm in diameter, at a distance of approximately 1.50mm from the edge of the specimen. The measured thickness at this point was approximately $2\mu\text{m}$, while the thickness of the coating on the flat surface was $16\mu\text{m}$. This is usually attributed to the fact that the depositing material may follow the electrical field lines terminating on all points of the cathode surface or more likely that it is scattered all over due to multiple collisions as it is traversing the plasma region. An additional reason of coating uniformity is that this method, using gaseous reactants, does not utilize any source of evaporation providing high flux of coating material towards the one of the specimen surface, as happens with conventional and reactive ion plating.

The examination of the surface topography of the coatings showed that it is not smooth. Nodules of different sizes (4 to $12\mu\text{m}$) are always present on the surface. As proved by electron probe microanalysis the composition of the nodules is the same as

that of the matrix. The roughness measurements of the surface gave values of centre line average (c.l.a.) between $0.32 \pm 0.02 \mu\text{m}$ and $0.84 \pm 0.03 \mu\text{m}$ and maximum peak-to-valley roughness between 2 and $5 \mu\text{m}$. If these roughness values are compared with the roughness values of the polished substrates which had a centre line average of $0.020 \pm 0.003 \mu\text{m}$, it can be said that this method does not provide finished surfaces as good as the starting ones.

Examining the properties of the coatings obtained it can be said in general that these change with composition. It was found that coatings containing low concentration of carbon (approximately 38%) had the lowest microhardness value measured ($850\text{VHN}_{20\text{g}}$), while as the concentration of carbon increased the microhardness values increased sharply and at concentrations above 52% in carbon the microhardness attained an almost constant value of between 2700 and $3000\text{VHN}_{20\text{g}}$. A possible explanation to these changes of microhardness values can be that the chlorine concentration which is constant (3-4%) for the whole series of samples produced distorts the lattice and creates a number of defects in the structure of titanium carbide which are counterbalanced by the increase of carbon concentration. Another possible explanation is that, the high content of carbon in the coating is obtained at high concentrations of acetylene in the reaction mixture and as explained in Chapter 6.3, this would increase the number of nucleation sites thus providing a very fine grained deposit. Fine grain materials always display

higher hardness than coarser ones of the same composition.

Investigating the influence of substrate hardness on the microhardness of the coatings it was found that, those prepared under the same glow discharge conditions and the same gas reaction mixtures on mild steel and on carburized steel showed the microhardness does not change. From this it is deduced that the microhardness measured is characteristic of the coating alone. It was also found that the coatings prepared under the same reaction mixture composition (30% in C_2H_2) and voltage (4kV) but different currents, showed a linear change at microhardness with the change of current employed. The material deposited at 80mA showed to be softer (1425VHN_{20g}), than that deposited at 200mA (3000VHN_{20g}). So the general conclusion is that the microhardness values of the coatings prepared are the same as those given in literature for titanium carbide, when high current and also high concentration of acetylene in reaction mixture are used.

The samples prepared to measure the friction coefficient of titanium carbide coatings when rubbed against stainless steel counterface showed that the wear of samples take place in a smooth asperity cutting mechanism without delamination or spallation which would accelerate the destruction of the worn coatings. The measured friction coefficient values vary between 0.18 and 0.28

which is the range of values accepted in the literature. The low friction coatings seem to be obtained when the reaction mixture contained high concentration of acetylene, which means that they contain more free carbon than those of high friction coatings according to the analytical results obtained by electron probe microanalysis.

Examining the influence of carbon content on the adhesion of the coatings on the substrate, it can be said that samples prepared from high concentration of acetylene in the reaction mixture (above 15%) and thus containing high concentration of carbon (above 52%) showed a tendency of spalling around the centre of the upper surface of the specimen, while films containing low concentrations of carbon (below 52%) did not spall. For evaluating quantitatively the adhesion of coatings, the scratch test method was followed. Thus the critical load value for each particular sample was defined (as described in Chapter 6.2). From the values obtained it can be seen that the adhesion of coatings which did not show any spalling effect, was lower than that corresponding to coatings which were spalled. This is because when spalling occurs some of the interfacial stresses would have been relieved and after aging, resistance to scratching of the remaining part of the coating would be expected to be higher. Samples prepared on carburized steel substrates showed no sign of spallation and the values obtained for adhesion were of the same order as the samples prepared on mild steel under the same discharge conditions and

reaction mixture composition. The reason that these samples did not show signs of spallation should be ascribed to the fact that their interface is free of the intermetallic brittle compound or that this is locally isolated. Thus the stresses accumulated in the interfacial region during deposition can not cause spallation during cooling as happens when the intermetallic compound is present. It was also found that coatings prepared under low voltage (3kV) keeping the other variables constant showed lower adhesion values, as it is expected from the theory of ion plating process.

Finally, it can be said that the objectives of this investigation set out in the introduction have been achieved, because:-

- a) the deposited material under the proper conditions of glow can be a crystalline form of titanium carbide and as such is "hard".
- b) when the proper glow discharge conditions or the proper steel substrate is used the coating adheres well without signs of spallation.
- c) the temperature at which the deposition is taking place is relatively low (500 to 600°C) and as such the steel substrate would not show irreversible changes of its volume and its shape, since it is below the phase transformation temperature of steel.
- d) the coating is uniformly distributed all over the surface without indications of corner build-up, and even narrow

blind holes are coated reasonably.

- e) the only requirement which seems to divert from the original target is the smoothness of the surface of the coatings obtained, because their roughness is worse than the roughness of the starting surfaces and as such does not guarantee use of them as produced coatings to high precision applications without prior machining.

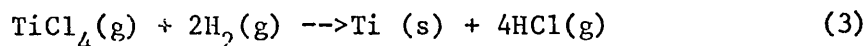
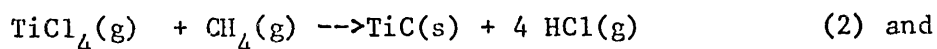
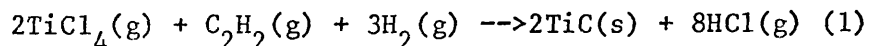
APPENDIX I

THERMODYNAMIC DATA ON THE REACTIONS ENCOUNTERED

IN THE PRESENT WORK

It is well known that coatings deposited from gaseous phases by the chemical vapour deposition method are dictated by the thermodynamic data of the reactions taking place. Knowledge of the changes of the free energy of a given reaction which will deposit a certain coating on a substrate, is very important because these determine the temperature range to which the substrate must be heated in order to start the deposition of the intended coating. Furthermore, the knowledge of the changes of the standard free energy determine the equilibrium constant and the feasibility of the reaction under consideration.

Making the assumption that the reactions which may deposit titanium carbide from titanium tetrachloride and methane or acetylene by the assistance of glow discharge are favourable kinetically and take place according to the principles of the thermodynamics, as happens with the corresponding reactions which take place in the chemical vapour deposition method, the change of free energy and the equilibrium constant under standard conditions, were calculated for the following reactions:

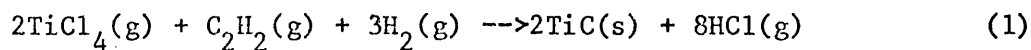


The basic thermodynamic data i.e. the standard enthalpies and entropies at 298°K and the heat capacities of the reagents involved were taken

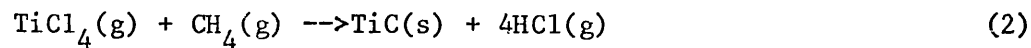
from Kubaschewski et al⁽⁸⁸⁾, except those which are related to acetylene which were taken from Stull et al⁽⁸⁹⁾. According to these calculations which have made due allowance for heat capacities, it was found that the starting temperatures (where $\Delta G_T^0 = 0$) of the above reactions are 803°K, 1200°K and 1500°K respectively. Table 22 shows the relevant free energies and equilibrium constants of these reactions at temperatures 750, 800, 900 and 1000°K. From the details shown on Table 22, it can be concluded that the temperature at which the reaction (1) starts is considerably lower than that of the reaction (2) and much lower than that of the reaction (3). Taking into account the fact that high temperatures cause changes to properties of steel substrates due to effects like softening it is important to keep the reaction temperature as low as possible in order to avoid such changes. For this reason the reaction (1) is more favourable than that of reaction (2). Formation of titanium carbide is favourable above 803°K from the gaseous reactions, titanium tetrachloride, acetylene and hydrogen, while no titanium metal is formed at all. As Archer⁽⁸³⁾ reports, the high stability of the titanium carbide results in a range of temperatures at which it can be formed in the absence of metallic titanium.

So based on the details of these calculations it can be seen that the energies required to be provided in order to start deposition of titanium carbide is smaller for the reaction (1) than for the reaction (2). Thus having as a guide the amount of energies required in order to reach the temperature at which the two reactions start, if they are carried out by chemical vapour deposition, it can be seen that it is preferable to use reaction (1) than reaction (2) in the case of chemical ion plating. In this case the obtained titanium carbide coating could be expected to be free of metallic titanium.

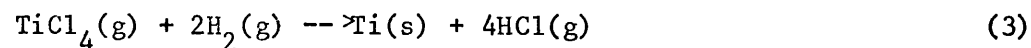
TABLE 22. Free energy changes and corresponding equilibrium constants for the given reactions.



Temperature °K	Free Energy Change $\Delta G \text{ Kcal mol}^{-1}$	Equilibrium constant Kp
750	+ 2.8	1.4×10^{-1}
800	+ 0.2	8.8×10^{-1}
900	- 5.0	1.7×10
1000	- 10.3	1.8×10^2



Temperature °K	Free Energy Change $\Delta G \text{ Kcal mol}^{-1}$	Equilibrium constant Kp
750	+ 26.0	2.6×10^{-8}
800	+ 23.1	4.7×10^{-7}
900	+ 17.4	5.9×10^{-5}
1000	+ 11.6	2.8×10^{-3}



Temperature °K	Free Energy Change $\Delta G \text{ Kcal mol}^{-1}$	Equilibrium constant Kp
750	+ 56.3	3.7×10^{-17}
800	+ 53.5	2.3×10^{-15}
900	+ 47.7	2.5×10^{-12}
1000	+ 41.8	7.1×10^{-10}

It should be noted that these arguments apply to species in their standard states whereas in chemical ion plating the reaction occurs under unknown non-standard states. However, it is reasonable to suppose the ranking order for reactions (1), (2) and (3) which apply to standard states may also apply to non-standard states. Thermodynamic data, are thermal data and therefore take no account of the possibility that reactants may be in electronically excited state produced in the glow discharge. Therefore, these thermodynamic data must be treated with caution.

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